THE INFLUENCE OF PHOSPHORUS FIRE RETARDANT REACTIVES ON THE THERMAL DEGRADATION OF POLYURETHANE

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SUMMARY

The object of this work was to prepare some polyurethanes which contained phosphorus and to observe the major features of their thermal degradation. If the mechanism of thermal degradation was revealed some fundamental reasons for the flame retardant properties of phosphorus might become evident.

Chapter 3 describes how phosphorus was incorporated in the backbone chain of the polyurethanes by copolymerisation of linear polyesters of phosphoric and phosphonic acids with methylene bis(4-phenylisocyanate) (M.B.P.I.) and the chain extender 1,4-butanediol (B.D.). Four polyurethanes, P.U.1, P.U.2, P.U.3 and P.U.4,were prepared using these phosphorus polyesters which had different structures and molecular weights. The polymers were then characterised chemically and spectroscopically and in the case of P.U.1 evidence presented to confirm its structure.

Before the thermal degradation of the polyurethanes was studied additional information was obtained from thermal analysis of poly-[butylene phenylphosphonate], the polyester used to prepare Polyurethane 1. The results in Chapter 5 supplement those in literature which describe the thermal degradation of the polyurethane, poly-[butylenemethylene bis(4-phenylcarbamate)] to allow a prediction from first principles of the reaction of P.U.1 to heat.

Many of the reactions of thermal degradation seen in poly-[butylenemethylene bis(4-phenylcarbamate)] and poly[butylene phenylphosphonate] occur in P.U.1; however Chapter 6 also highlights new reactions and interactions which occur in the polymer. Further from the thermal degradation of five samples of Polyurethane 1 each containing a different proportion of hard segment (M.B.P.I. + B.D.) and polyester it was evident that phosphorus enhances one of three standard mechanisms of decomposition of urethane.

In Chapter 7 the effect which small modifications to the structure of the phosphorus polyester in the polyurethane backbone chain have on the overall thermal degradation of the polymer was investigated. Some changes believed to be beneficial to the flame resistance of the polyurethane were noted and the phosphorus, active in the form of an acid during thermal degradation, seen to promote decomposition at lower temperatures.

The final chapter has discussed the pure and applied problems of creating and testing non-inflammable plastics. Rather than suggest a solution the author has had to be content to explain the hurdles confronting scientists who are required to predict the performance of polymeric materials using only results from small scale laboratory experiments.

Finally suggestions for future work in this field are offered both out of academic interest and as potential areas of practical importance.

CHAPTER 1

INTRODUCTION

The reaction between alcohol and isocyanate or condensation of amine with chloroformate produces urethanes,

$$\underset{\text{(isocyanate)}}{R\text{-}N=C=O} + \underset{\text{(alcohol)}}{H\text{-}O\text{-}R'} \rightarrow \underset{\text{(urethane)}}{R\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R'}$$

characterised by the structure $-\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O-$. The corresponding difunctional species react similarly to form polymers, namely polyurethanes which have been found to have great commercial value.

The interesting physical properties of polyurethanes can be extended by copolymerisation with polyester or polyether but although the resulting elastomers or foams may contain comparatively small amounts of urethane structures the description has been retained.

So the term "polyurethane" or recently "urethane" now describes a large set of man-made polymers which may bear little similarity to each other save the presence of some urethane links in the molecular backbone.

1.1 HISTORY

Although polyurethanes represent a large and important section of the family of man-made polymers and are associated with the twentieth century their precursors, the isocyanates, were the subject of investigation by Wurtz as early as 1849[1]. Carbamates now commonly called urethanes were prepared as derivatives of monofunctional isocyanates and alcohols and their stability to heat first measured in 1850[2].

However the modern polyurethane emerged in Germany during the years preceding the second world war when Otto Bayer developed linear

polymers suitable as plastics, fibres and bristles. Similar work was starting in America under Cattin but the initiative remained with Germany during the war when Bayer found polyurethanes useful as rigid foams, adhesives and coatings and Hoff and Wicker demonstrated that polycondensation of diamines with bischloroformates offered a new route to the material.

After 1945 the commercial importance of polyurethane was declared by American industry, in particular the aircraft companies who made massive investments in research and development using expertise from Germany. The popular diisocyanate monomer at this time comprised a mixture of isomers of toluene diisocyanate, T.D.I., but in the 1950's the Imperial Chemical Industries discovered that the less harmful methylene bis(4-phenylisocyanate),M.B.P.I., produced equally useful polymers.

Although I.C.I. developed the use of this cheap alternative, major commercial progress was achieved from experiments with different glycols and incorporating polyesters in the polyurethane structure. Flexible foams prepared from polyesters had been studied in Germany by Bayer and appeared in America from 1954. These polyesterurethanes were also adapted for use as coatings, elastomers and adhesives. However these new types of polyurethanes did not threaten to replace traditional materials.

Polyethers soon replaced polyesters as a cheaper alternative and after exploiting the many combinations of glycols, triols, polyols and polyether glycols in polyurethane production many products became commercially available including flexible foams whose physical properties and cost were superior to those of foam rubber. This latter success assured a world-wide market for polyurethanes and improvements to cost, performance and applications have continued from that time.

Fluoro-chloro-hydrocarbon blowing agents were first used in 1959 leading to rigid polyurethane foams with improved thermal properties. Rigid foam laminates became available in the 1960's. Despite the excellent physical properties of polyurethane elastomers and fibers, financial considerations have prevented them making the same impact as polyurethane foams. However these materials have developed on more modest scales for specialised uses. Some of the applications of polyurethane are mentioned in Table 1.i.

Table 1.i: Applications of Polyurethane

Polyurethane	Application
Flexible Foam	Furniture, Bedding, Transportation, Clothing, Carpets (backing), Filters, Sponges, Construction Industry (insulation; laminates), Packaging
Rigid Foam	Refridgeration Insulation, Pipe Insulation, Packaging, Structural, Void Filling (aircraft; shipping)
Elastomer	Tyres, Shoe Soles, Friction Drive Belts, Rollers, Gaskets, Seals, Electrical Insulation
Coating	Coating Wood, Concrete, Metal, Fabrics
Adhesive	Possible for any Surface-to-Surface by Planning Molecular Structure
Fibres	Replacement of Polyamides with Improved Electrical, Chemical, Weathering properties

1.2 SOCIAL ASPECTS OF THE POLYURETHANE IMPACT

The properties and versatility of polyurethanes explain in part the success and increase in demand they have enjoyed over the past two decades. However problems associated with the industry and the material have increased on a similar scale. Recent fire tragedies in Britain have focussed public attention on the flammable nature of urethane and when the full extent of public dependence on polyurethanes in everyday life was realised it is hardly surprising that demands were made for stronger legislation to govern standards of flame resistance.

The Fire Hazard

One argument on this topic is supported (for whatever motive) by the urethane industry who insist that too few exhaustive surveys are available to accuse any material of being especially hazardous. On the contrary statistics do not suggest that polyurethanes are particularly dangerous[3]. Both American and British surveys indicate that while usage of urethanes has risen sharply during the last 20 years the ratio of deaths to casualties in fires has remained virtually constant.

An explanation for this observation may be in the actual location of polyurethanes in everyday use. For example polyurethane foam is known to burn vigorously evolving toxic gases. However rigid foam laminates used as building materials are unlikely to be the source of a fire and seldom suffer more than scorching[4]. Similarly flexible foams used in upholstery offer very little threat to safety if a suitable flame resistant covering is present[5].

Finally some interesting facts which are available to the public show that factors completely divorced from the nature of materials present in buildings are far more significant in determining fire hazard levels and fatalities. These are as follows.

(a) Despite fire regulations the design of buildings still reflects an ignorance of the way in which fire can spread i.e. through ventilation shafts, service ducts and externally between windows[6].

(b) Domestic fires involving modern furniture develop slowly but spread quickly giving 2-3 minutes to escape. Deaths from choking and intoxication are more common than by burns[7].

(c) Statistics from post mortems confirm death by poisoning or choking occurs more often than by burns. However 59% of cases studied had alcohol levels which would render victims incapable of escape[8].

So by comparison it seems polyurethanes normally contribute less to the potential fire hazard in buildings and dwellings than feared. However their flammability must be significant to safety when large amounts are present in confined spaces and in contact with human beings and human fallability. Perhaps stricter regulations are justified to control the materials kept in furniture department stores, or used in passenger trains or aeroplanes. Certainly the growing urethane industry in America has had to respect the Amended Flammable Fabrics Act of Congress while the National Bureau of Standards has designed various A.S.T.M. tests to try to assess fire properties of modern materials. In Britain legislation to ensure stricter regulations concerning the flammability of polyurethanes is expected soon and has been precipitated in no small way by public opinion of the substance and its "associated hazards".

The social impact of polyurethane materials then has been two-fold. Since the 1950's these products have found increasing applications and experienced a growing demand but their popularity has been tempered in the last decade by under-publicised health hazards during manufacture and what may be over-reaction to the fire hazard.

1.3 RESEARCH IN FLAME RESISTANCE

Commercial companies have responded well to public demand and legislation calling for improvements. Much effort has been made particularly in the field of polyurethane foams to increase their fire resistance. Many approaches have been investigated, the traditional method involving the use of additives or reactives while more recently the effect of structure modifications has attracted interest. The more promising materials which have been developed can be assessed by a variety of convenient laboratory methods designed to measure the following properties,

(i) ease of ignition
(ii) speed of flame spread,
(iii) evolution of heat,
(iv) smoke,
(v) toxic gases,
(vi) ease of extinction,

but it is at this stage of the research programme that serious problems are encountered. Although techniques claiming to indicate the flame resistance of plastics exist and many of these have been standardised by the National Bureau of Standards, results from such tests do not consistently reflect the large scale fire performances of the materials.

At the 5th International Fire Protection Seminar, 1976, after extensive laboratory and full scale experiments, H. Zorgmann stated that

> "No correlation was found between the fire behaviour of the roof as a whole and the classification of bare surfaces of the insulating slabs themselves in standard fire tests approved to predict the performance of wall and ceiling linings in developing fires".[9]

The Burning Cycle

So formidable problems must be overcome to remove much of the empirical nature of research and development in this field. A fundamental requirement for successful research in flame resistant polymers is an understanding of the mechanisms which operate when such material "catches fire" and "burns".

Plastics being solids do not burn but vapours which they can release do. Therefore Grassie[10] has described a burning polymer as simply a source of volatile fuel which burns, the inflammable fuel arising from thermal degradation of the polymer. The temperature required for this degradation is a characteristic of the polymer and can be 200-250° for polyurethane. Thomas and Bullen[11] describe similar circumstances and argue that early burning at least constitutes consumption "of volatile material emitted as a result of thermal decomposition" near a flame. They calculate the diffusion of volatile material out of a polymer is sufficient initially to exclude oxygen from the degrading region.

If a system burns unaided some sort of thermal feedback must operate thereby completing what is termed the Burning Cycle[10,12]. This is shown in Figure 1.I. Clearly to maintain the cycle and the burning process the quantity of heat transferred to the polymer in step III must be greater or equal to that required for thermal degradation and ignition of inflammable products, the sum of I and II.

Methods of Retardation

To extinguish a burning polymer the burning cycle must be interrupted at one or more of its stages and on this principle four approaches have been used to create self-extinguishing plastics.

1. Use of Additives: The most obvious method of altering the properties of a polymer is to produce a blend with a solid or liquid which would be present during the initial stage of "burning" to decompose with the plastic.

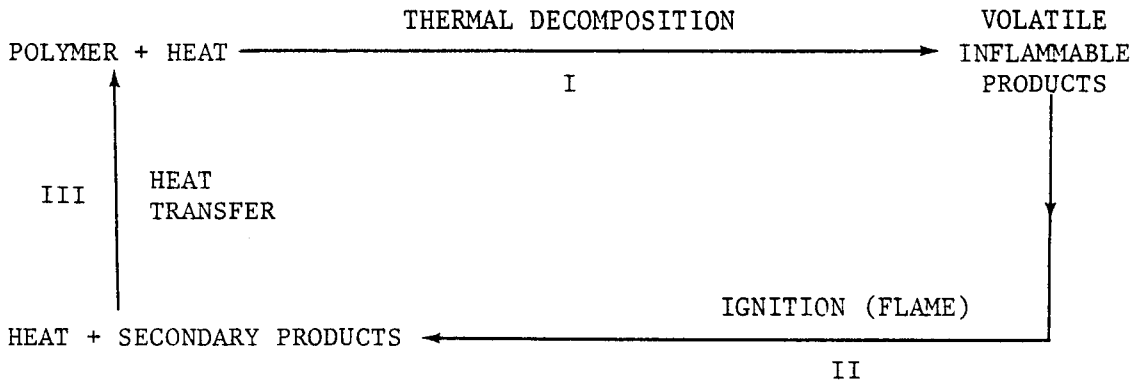


Figure 1.I: The Burning Cycle

2. Use of Reactives: A more elegant approach involves a flame retardant agent bonded to or part of the polymer backbone chain. This technique ensures the material suffers smaller losses of agent through weathering or early volatilisation by heating.
3. Structural Modification: Modifications to the chemical structures of some polymers have been found which do not seriously affect physical properties yet improve fire resistance.
4. Substitution by Entirely New Substances: New materials have been developed which may replace polyurethane in some applications. For example inorganic foams, basically sheets of silica which have been inflated by a blowing agent, have the advantage of lower cost and are non-inflammable.

The most widely used methods of imparting flame resistance involve reactives or additives. These species usually contain halogen or phosphorus or a combination of both. If halogen is present in a burning polymer much of it will escape as volatile products of degradation. However since these halogenated products are usually non-inflammable this has a suppressive effect on a flame, clearly interrupting the burning cycle at step II. Halogens are said to operate in the vapour phase[13,14].

When inorganic elements such as phosphorus form part of a polymer the formation of char by heating becomes more facile. In effect an insulative layer forms around the sample which impedes further thermal degradation and breaks the cycle at step III. Phosphorus is said to operate in the solid phase. Some examples of flame retarding materials and the stage of burning most strongly affected are shown in Table 1.ii.

Synergism

Early attempts to compromise or combine the properties of various flame retardant species in one polymer soon led to evidence of synergism between certain elements. In this context a SYNERGISTIC EFFECT is said to operate when a greater flame retardancy is observed than would otherwise be expected from the additive effects of the individual reagents. Several authors have reported evidence believed to point to synergism between phosphorus and bromine and between phosphorus and nitrogen[13-15] and research into additives and reactives appears to favour combinations as limits to flame resistance are being reached in some cases.

Table 1.ii: Flame Retardant Materials

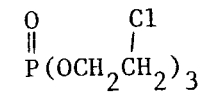
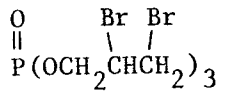
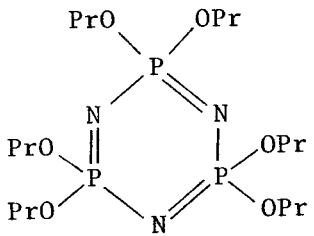
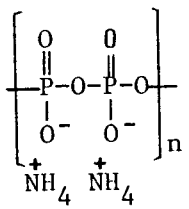
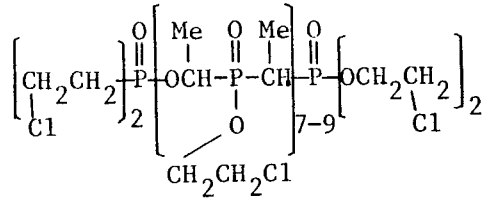
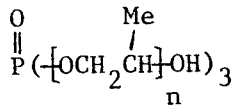
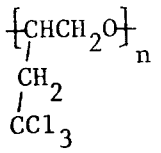
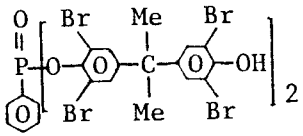
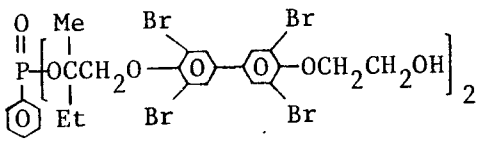
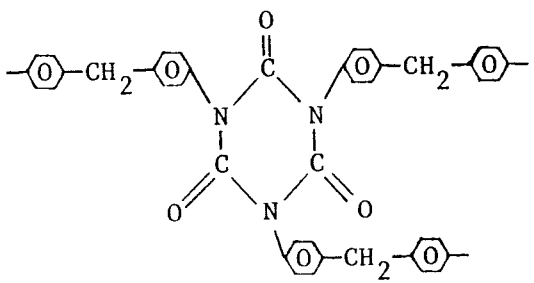
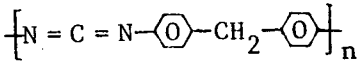
Classification	Name	Structure	Step of Burning Cycle Affected
ADDITIVE	Tris(chloroethyl)phosphate		II, III
	Tris(2,3 dibromopropyl)phosphate (FIREMASTER)		II, III
	Hexapropoxyphosphazene		III
	Ammonium Polyphosphate (PHOSCHEK)		III
	PHOSGARD		II, III

Table 1.ii (continued)

REACTIVE	Oxypropylated Phosphoric Acid		III
	Polytrichlorobutylene oxide		II
	Halogenated Polyphosphonates C.A. 85; P 144599e		II, III
	C.A. 83; P 194561r		II, III
STRUCTURAL CHANGES	Polyisocyanurates		III
	Polycarbodiimides		III

1.4 THERMAL DEGRADATION OF POLYURETHANE

As mentioned previously the temperatures at which polyurethane degrades are relatively low. The second parameter which determines the flammability of a polymer is the quantity and nature of volatile products from degradation.

The work carried out at this University on thermal degradation of polymers seems especially relevant to this field of study since the temperatures of thermal degradation of polyurethanes are easily reproduced and techniques are available to identify the crucial volatile products of degradation. The degradation of polyurethanes in absence and in presence of phosphorus flame retardants would allow mechanisms of thermal degradation to be postulated and thereby provide insight into the mode of action of the retardant.

The remainder of this chapter describes the work which has been reported on the thermal degradation of polyurethanes from this laboratory and the remainder of this thesis describes attempts to elucidate mechanisms which operate during thermal degradation of polyurethanes which contain copolymerised phosphorus polyesters.

Grassie and Zulfiqar have studied the thermal degradation of three systems, namely

I Poly[butylenemethylene bis(4-phenylcarbamate)] [16]

II Poly[butylenemethylene bis(4-phenylcarbamate)]: Ammonium Polyphosphate Blend [10]

III A Polyesterurethane [17]

I The thermal degradation of the polyurethane from 1,4 butanediol and methylene bis(4-phenylisocyanate) begins to occur above 200° and initially constitutes depolymerisation to the monomers. However a variety of secondary reactions occur which lead to several volatile products and residual carbodiimide and urea structures. A mechanism has been suggested which accounts for the principal features of the degradation and is shown in Figure 1.II.

II The influence of the additive, ammonium polyphosphate on the thermal degradation of the polyurethane described above is considerable even if present in small proportions. The products of thermal degradation of the polyurethane in presence and absence of the additive are recorded in Table 1.iii. The corresponding modifications to the mechanism of degradation have been made in Figure 1.III.

III The final polyurethane system to be investigated comprised eight

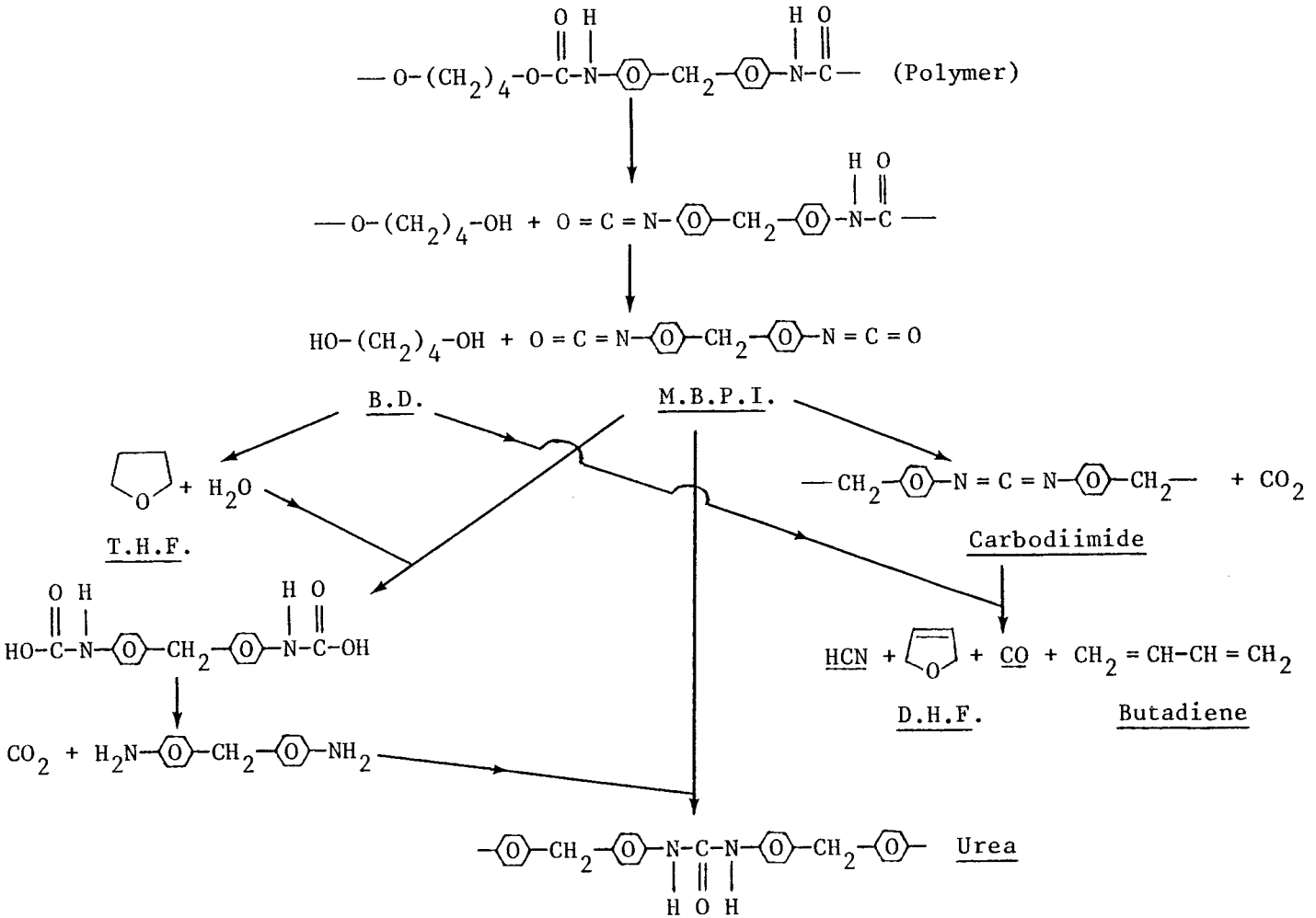
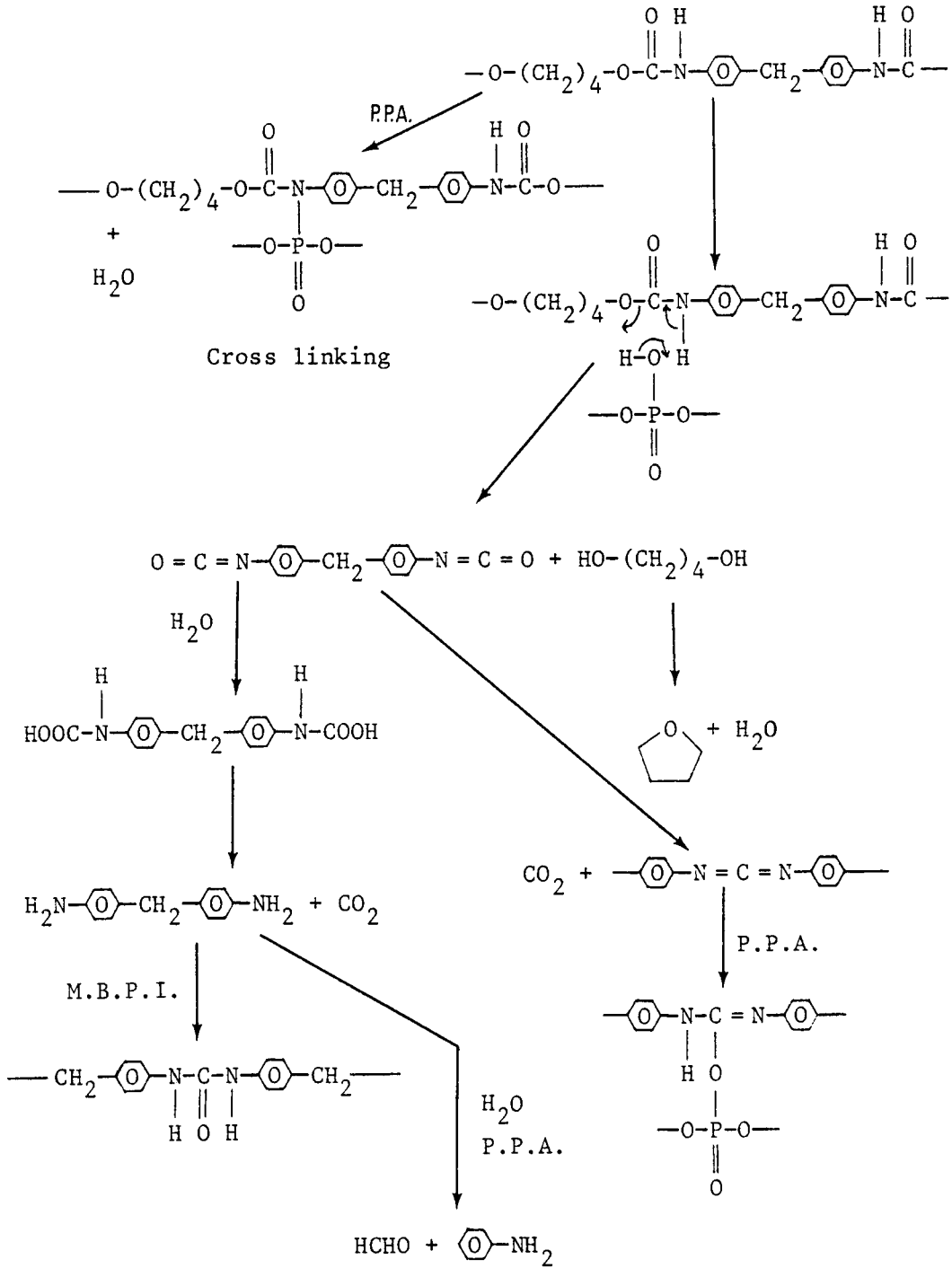


Figure 1.II: Thermal Degradation of Poly[butylene methylene bis(4-phenylcarbamate)]

Table 1.iii: Products and Structural Change on Degradation of Polyurethane

Poly[butylenemethylene bis(4-phenylcarbamate)]	Abbreviation	Polyurethane : Ammonium Polyphosphate
1,4 Butanediol	B.D.	Absent
Methylene bis(4-phenylisocyanate)	M.B.P.I.	Reduced
Carbon Dioxide		Present
Butadiene (minor)		Absent
Tetrahydrofuran	T.H.F.	Present (increased)
Dihydrofuran (minor)	D.H.F.	Absent
Water		Present
Hydrogen cyanide	HCN	Absent
Carbon Monoxide	CO	Absent
Loss of N-H (urethane)		Present
Formation of Carbodiimide	C.D.I.	Present (reduced)
Formation of Urea		Present
		Aniline
		Formaldehyde
		C = N structures
		P-O-C structures
		Large Residual Char



P.P.A. = Polyphosphoric Acid

Figure 1.III: Thermal Degradation of Polyurethane: Ammonium Polyphosphate Blend

polymers based on poly[butylenemethylene bis(4-phenylcarbamate)] but each containing a unique proportion of copolymerised linear polyester soft segment. The polyester segment was the condensation product of adipic acid, ethylene glycol and propylene glycol, with a molecular weight of ~9000.

Thermal analysis has shown the urethane regions (hard segments) which contain high concentrations of polymerised methylene bis(4-phenylisocyanate) and 1,4-butanediol are less stable to heat than the soft segments of polyester. Most of the thermal degradation results can be accounted for in terms of independent degradation of the segments or domains in the polyesterurethane. However some interaction does occur. The production of carbodiimide is suppressed and relative amounts of amine, diisocyanate and urea indicate that acid catalysed degradation also occurs.

CHAPTER 2

EXPERIMENTAL

2.1 SYNTHESIS OF POLYURETHANES

A large proportion of this work was devoted to synthesis of polyurethanes which contain phosphorus. Consequently it was felt that details of the preparation should be reported in a separate section. Chapter 3 describes the synthesis.

2.2 POLYMER CHARACTERISATION

Infrared Spectroscopy

Infrared spectra were recorded either on a Perkin Elmer 197 or on a Perkin Elmer 257 grating infrared spectrophotometer.

Polyurethane samples were prepared as thin films on sodium chloride discs. The films were cast from dimethylformamide solution and kept under vacuum at 70-100^{o} for 2-3 days to remove traces of solvent.

Each phosphorus polyol and prepolymer was dissolved in chloroform and quickly cast as a film on a salt plate. Their spectra were recorded after drying for several hours.

Model compounds were studied either as pure liquids or in nujol mulls.

Nuclear Magnetic Resonance Spectroscopy (N.M.R.)

A Perkin Elmer R32 instrument was used to examine the polymers and model compounds.

Perdeuterodimethylsulphoxide proved to be a useful solvent for polyurethanes. The phosphorus polyols and model compounds were run in $CDCl_3$ solution.

All chemical shifts were measured with respect to an internal standard, tetramethylsilane (T.M.S.).

Molecular Weight

Osmotic Pressure Measurement: The number average molecular weight of four polyurethanes was measured using a Mechrolab 501 high speed membrane osmometer equipped with a Sylvania 300 cellophane membrane. Samples were dissolved in dry distilled dimethylformamide (D.M.F.) to several concentrations of approximately 1% w/v and measurements taken at 25°. The operative lifetime of the membrane was less than one week in D.M.F.

The number average molecular weights of three phosphorus polyols were determined osmotically using a Mechrolab 301A Vapour Pressure Osmometer. Chloroform treated to remove ethanol inhibitor was used as solvent. Several solutions of concentrations between 0.5 and 0.005 g/ml were used for measurement at 25°.

End Group Analysis: Several methods have been reported by which the number of functional groups on an oligomer can be counted. When the number of groups on each molecule is already known, the molecular weight can be calculated. The phosphorus polyol, with terminal hydroxyl groups, was suitable for this type of analysis.

The method outlined by Sorenson and Campbell[18] was followed. Reaction of 1.05 ml phenylisocyanate with 2-3 g of sample in 20 ml chlorobenzene was followed by direct addition from pipette of 1 ml n-butylamine. The mixture was then titrated with N/10 hydrochloric acid to a neutral end-point indicated by bromophenol blue.

The number average molecular weight, M_n of the polyol was calculated from the equation,

$$M_n = \frac{\text{Weight of Sample, g}}{\left[\frac{(\text{Volume HCl for sample} - \text{Volume HCl for blank}) \times N/10 \div 1000}{2}\right]}$$

Microanalysis

Each polyurethane and polyol was analysed for its phosphorus content. Samples were combusted and titrated with thorium nitrate solution to an end point indicated by a solochrome cyanine R/methylene blue mixture. Triphenylphosphine was used as the standard.

The abundance of carbon, nitrogen and hydrogen in the polyurethanes was also measured using a Carlo Erba Elemental Analyzer 1106. Samples were flash combusted to CO_2, H_2O and N_2 which were separated and measured by quantitative gas-liquid chromatography.

Thin Layer Chromatography

The macrodiisocyanate prepolymer and phosphorus pholyol were analysed to determine the efficiency of end-capping with methylene bis(4-phenylisocyanate).

Samples were dissolved in chloroform and spotted onto Kieselgel $60F_{254}$ plastic T.L.C. plates. The chromatogram was run in a tank of chloroform and the result studied under ultraviolet lamp.

2.3 THERMAL VOLATILISATION ANALYSIS (T.V.A.)

The Simple T.V.A.

It has proved possible to record the reaction of a sample to a programmed temperature rise by continuously monitoring the pressure of gases released. Reproducible and useful information can be obtained by this technique of thermal volatilisation. The applications and advantages have been described[19].

Differential Condensation T.V.A.

The simple T.V.A. system has been developed by several workers, in particular McNeill, to produce a more powerful analytical tool, differential condensation thermal volatilisation[20]. This exploits the characteristic condensation properties of the volatile products from thermal degradation of a sample.

Figure 2.I shows schematically the apparatus required to demonstrate differential condensation thermal volatilisation.

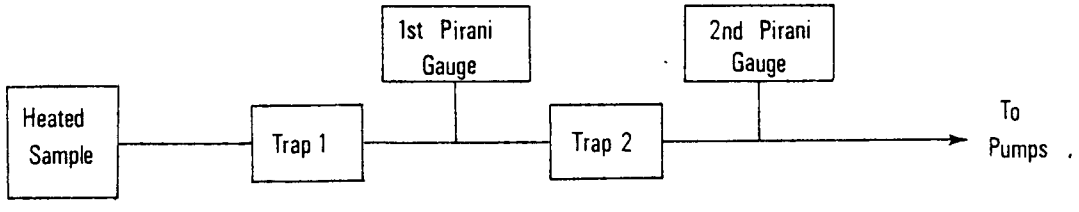


Figure 2.I

A vacuum line is continuously pumped. Trap 2 is maintained at -196° and trap 1 at a temperature higher than this but below ambient temperature. Volatile degradation products are released as the sample is heated but only the pressure of those sufficiently volatile to pass through the first trap will be recorded by the first pirani gauge. The second pirani gauge records the presence of material not condensed at -196°.

When four temperatures 0°, -45°, -75° and -100° are chosen for the first trap a wide range of responses can be recorded for the same material[21]. In practice this need not entail four separate experiments since all the information can be collected simultaneously using the system shown in Figure 2.II.

This system was used to obtain thermograms of all materials of interest in this work. Some details of its operation will now be described.

Operating Conditions

Continuous pumping maintained a high vacuum of 10^{-4}-10^{-1} torr throughout the heating programme. It was possible to maintain trap temperatures as indicated within $\pm 2^{\circ}$ for the duration of the experiment.

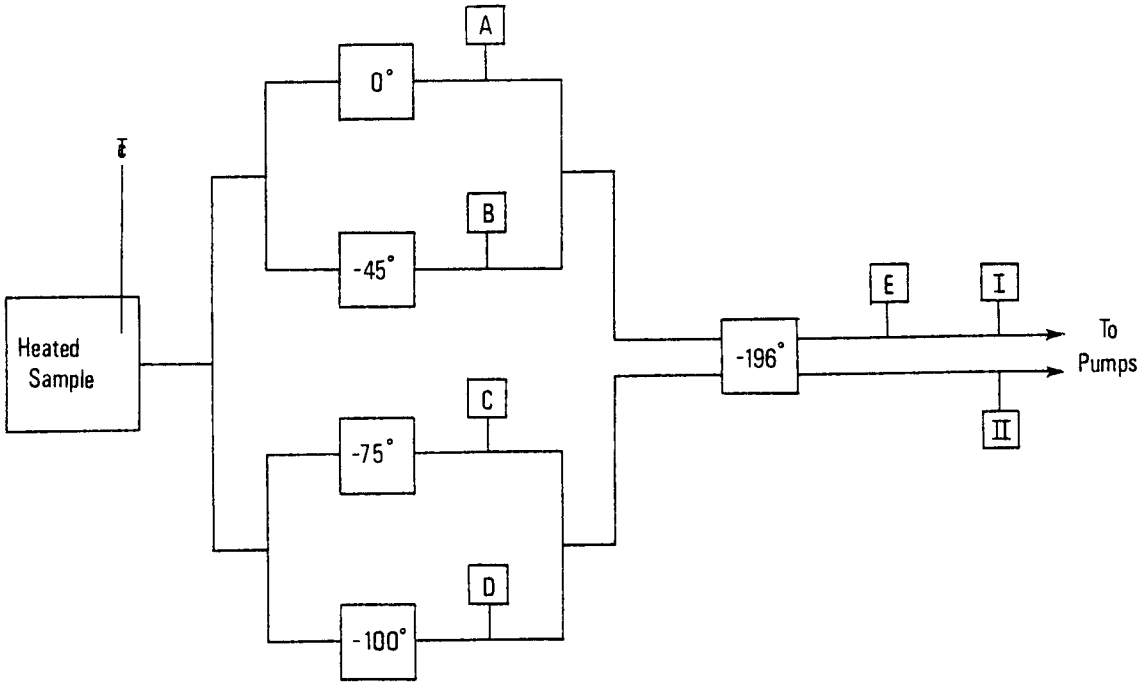
A multichannel recorder was used to plot the responses of the five pirani gauges and the current from a chromel-alumel thermocouple in the oven, close to the sample. Between 40 and 50 mg of sample in powder form were most successful.

A modified Perkin Elmer F11 oven equipped with a linear temperature programmer was used to heat the sample. The oven was programmed to heat at a rate of 10° per minute from room temperature to 500° although a variety of rates and isothermal temperatures could be selected.

Since the sample was housed in a cylindrical glass degradation tube within the oven, a temperature gradient between oven and sample was observed during programmed heating. To measure the temperature difference a second thermocouple was appropriately positioned inside the tube during a mock thermal programme. Temperatures recorded for a real situation were then corrected.

Products from Thermal Degradation

Each product of a thermal volatilisation analysis falls into one of four classes, which defines its volatility in the system. The thermal degradation product is either



A, B, C, D, E = Pirani gauges, T = Thermocouple,
I, II = Collection points
Pirani Gauges A-D equidistant to oven and to -196° trap

Figure 2.II: Differential Condensation T.V.A. Apparatus

(a) an involatile residue,

(b) volatile at degradation temperatures but involatile at ambient temperatures (cold ring fraction),

(c) volatile at ambient temperature but involatile at the cold traps (condensables), or

(d) volatile even at -196^{o} (non-condensables).

Subambient T.V.A.

It is important to identify the products of thermal degradation. As suggested earlier, the condensables from a T.V.A. can be collected at a point on the line and removed for study. However in most cases a mixture of products is involved which can make identification difficult.

The need to separate and isolate the products has been solved by a distillation technique described by Ackerman and McGill[22] and by McNeill et al.[23]. The latter have applied the technique to thermal degradation products and have named it Subambient Thermal Volatilisation Analysis. The equipment, which can be used independently or coupled to a standard T.V.A. line, is shown in Figure 2.III.

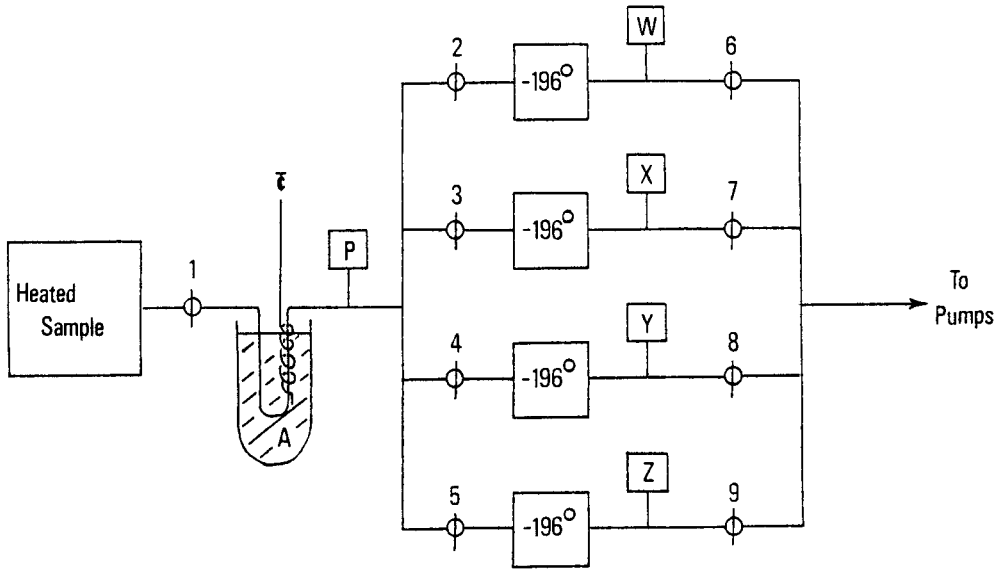
A high vacuum is first achieved and maintained in the system. The traps in the parallel limbs are kept at -196^{o} while the polyethylene glycol jacket surrounding the first trap is cooled to the same temperature. The volatile degradation products released on heating the sample are condensed in the first trap.

Once the thermal degradation programme is complete stopcocks 1, 3, 4 and 5 are closed and the polyethylene glycol jacket allowed to warm up to room temperature. The temperature is monitored by an external thermocouple. The products will distil into the second trap at temperatures dependent upon their volatilities. The pressure and temperature are recorded as functions of time.

The type of trace obtained is shown in Figure 2.IV.

The subambient trace shows the minimum number of volatile fractions which have distilled into the second trap. If the first trap is cooled again and the condensables returned to it, the experiment can be repeated. On this occasion the remainder of the system can be used to separate and collect individual fractions. As each product escapes from the polyethylene glycol trap a different limb of the parallel arrangement is opened to receive it. Thereafter the limb is closed and the trapped condensable passed to the collection point for analysis.

In this work samples ranging from 7 to 250 mg were tested using this technique. Powders were used when possible.



A = Polyethylene Glycol Jacket, T = Thermocouple, P = Pirani Gauge, W, X, Y, Z = Collection Points, 1-9 = Stopcocks

Figure 2.III: Subambient T.V.A. Apparatus

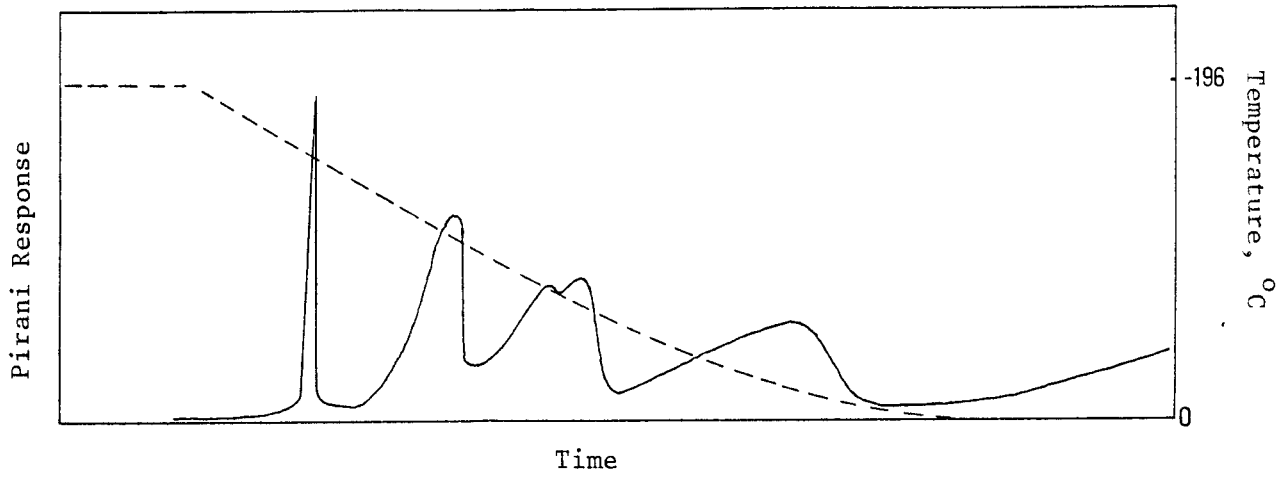


Figure 2.IV: Typical Subambient T.V.A. Trace

2.4 DIFFERENTIAL THERMAL ANALYSIS (D.T.A.)

The difference in temperature (ΔT) between a sample and an inert reference was measured and recorded as a function of temperature by a Du Pont 900 instrument. A powdered sample weighing about 10 mg was used. Dynamic nitrogen with a flow rate of 60 ml/minute provided an inert atmosphere. The usual heating rate of 10^{o}/minute from 20^{o} to 500^{o} was used.

2.5 DIFFERENTIAL SCANNING CALORIMETRY (D.S.C.)

The energies required to maintain a sample and reference at the same temperatures during a programmed temperature rise will not be identical. A Du Pont 910 differential scanning calorimeter was used to measure the energy difference.

Approximately 5 mg of the sample in powder form was placed in an aluminium D.S.C. pan. The reference was an empty pan. Again a nitrogen atmosphere with a flow rate of 60 ml/minute was chosen while temperatures were raised by 10^{o} per minute to 500^{o}.

The technique provides a quantitative measure of heat flow in and out of the sample during the programme. Thus when required, heats of reactions can be calculated using the calibration coefficient of the D.S.C. cell.

Using a sample of pure indium (ΔH fusion = 28.47 j/g), the coefficient was measured to be 0.0749 mW/mV.

2.6 THERMAL GRAVIMETRIC ANALYSIS (T.G.A.)

A Du Pont 951 thermogravimetric analyzer was operated between ambient temperature and 600^{o} at a programmed rate of 10^{o} per minute and the change in weight in dry dynamic nitrogen recorded as a function of temperature. A Du Pont 950 T.G. analyzer was used to obtain the thermogram of a sample under partial vacuum (0.5-1.0 torr). In each case 5-10 mg samples were used.

2.7 SEALED SYSTEM DEGRADATION

Thermal degradation of a mixture or blend can present a problem when one or more of the components is volatile at elevated temperatures since material can be lost before true degradation occurs.

In this case a simple reaction tube with break-seal and constriction was used to contain the material. The design used in this work is

shown in Figure 2.V.

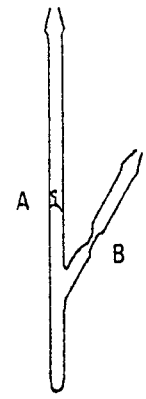


Figure 2.V

The sample was introduced via constriction B and the tube sealed at that point under high vacuum. The sealed system was small enough to fit inside a Perkin Elmer F11 oven.

After heating, volatile products were released through the break-seal A and collected for analysis. The residue was recovered by fracturing the tube.

2.8 ANALYSIS OF DEGRADATION PRODUCTS

Infrared Methods

Infrared spectra were recorded by Perkin Elmer 197 and Perkin Elmer 257 spectrophotometers.

Polymer residue after thermal degradation was studied in three forms: as a thin film, in a KBr pellet or as a nujol mull.

Any product found at the cold ring of the degradation tube was examined as a thin film, KBr pellet or nujol mull according to convenience.

The infrared spectra of volatile products were recorded in the gaseous or liquid phase. Gas cells were 6 cm in length with 13 mm diameter NaCl windows.

Quantitative Measurements

Infrared spectroscopy was used to measure the amount of carbon dioxide and tetrahydrofuran (T.H.F.) in the volatile degradation products of the polymers. The problems of this experiment are explained

in simple terms by Alpert, Keiser and Szymanski[24] . A brief account of theoretical and practical aspects involved will be given.

Beer's Law states that the absorbance, A, of a beam of radiation by a gas is proportional to the path length and concentration of that gas. That is

$$A = \log P_0/P = a.b.c$$

P_0 = Incident Radiation Intensity
P = Transmitted Radiation Intensity
a = Absorptivity of sample at particular wavelength (a constant)
b = Path Length
c = Partial Pressure.

Gases in an infrared cell can be regarded as non-interacting which allows the ideal gas law

$$P.V = n.R.T$$ to operate.

P = Partial Pressure
V = Volume
n = Number of Moles of Gas
R = Gas Constant
T = Absolute Temperature.

Thus a relationship exists between absorbance and the amount of gas.

A gas cell of known volume was used. It was calibrated for each gas by constructing a graph of optical density against pressure. The apparatus used to construct the calibration graph is shown in Figure 2.VI.

When stopcocks 1 and 6 are closed, CO_2 or T.H.F. are introduced into the cell from the reservoir. The pressure is measured on the mercury manometer. From the infrared spectrum the optical density of a particular absorption band at that pressure can be measured. The process is repeated using various pressures until a graph of pressure versus optical density can be drawn accurately. The absorption bands of carbon dioxide at 2344 cm^{-1} of tetrahydrofuran at 918 cm^{-1} were used.

Mass Spectrometry (M.S.)

A mass spectrometer model AEI MS 12 with Micromass 2S8 console was used to measure the molecular weight of the products of thermal degradation. Solid, liquid and gaseous products were studied.

When compounds with a mass below 200 were suspected, the smaller

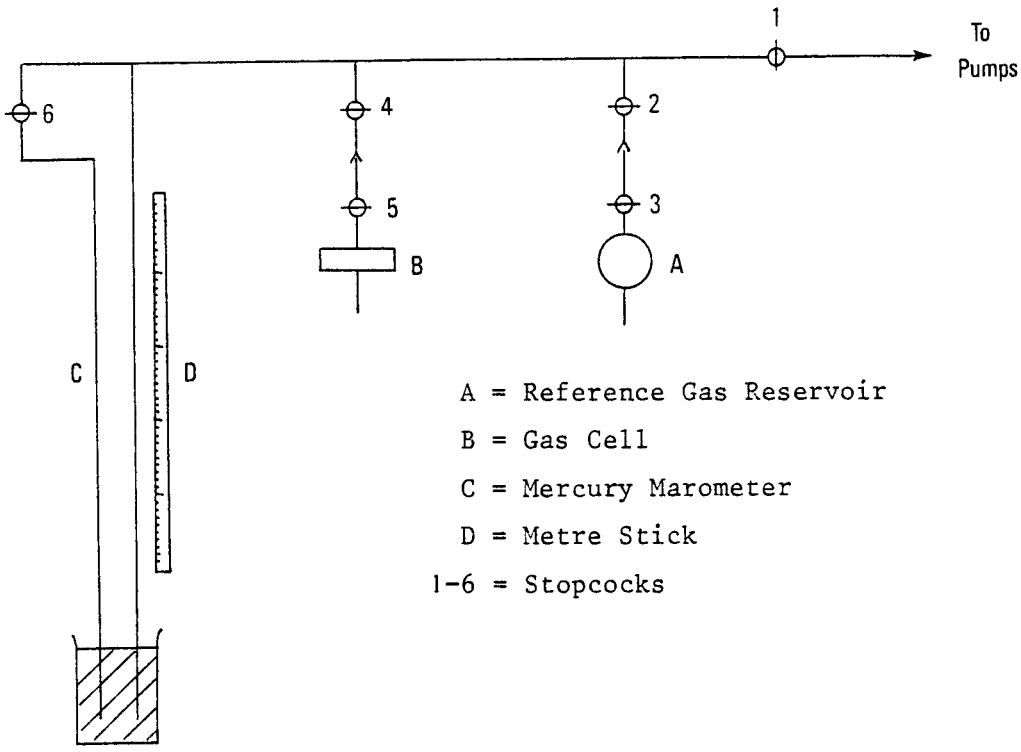


Figure 2.VI: Quantitative Gas Analysis Apparatus

Micromass QX 200 mass spectrometer was employed. This has the advantage that it may be directly coupled to the subambient T.V. apparatus so that external handling of the degradation products is obviated.

Gas-Liquid Chromatography (G.L.C.)

Subambient fractionation cannot guarantee to separate all volatile products of degradation since some may have similar boiling points. Gas-liquid chromatography of combined condensable fractions proved to be more efficient and assist identification.

Samples were dissolved in either acetone or ether prior to injection. A Perkin Elmer F11 flame ionisation gas chromatograph was operated with three different columns at various isothermal settings.

The conditions are summarised in Table 2.i.

Table 2.i

Column Length (ft) × Internal Diameter (in)	Column Packing	Operating Temperature, ^{o}C	Carrier Gas, Pressure lb/in^2
10 × 1/4	1% OV-1 on Chromosorb	100, 130	N_2, 18
6 × 1/4	10% Microwax on Chromosorb	70, 100, 130	N_2, 18
10 × 1/4	5% Free Fatty Acid Phase on Chromosorb	75	N_2, 18

Gas Chromatography - Mass Spectrometry (G.C.M.S.)

The most powerful analytical tool was an AEI MS 30 mass spectrometer interfaced with a PYE 104 gas chromatograph via a single stage glass jet separator. This was used to separate mixtures of high boiling point condensables. The chromatograph used helium carrier gas and operated at 130^{o} with a 9 ft column of 3% OV-1 on chromosorb.

Nuclear Magnetic Resonance Spectroscopy (N.M.R.)

Proton N.M.R. spectra were recorded on two instruments, the Varian T60 and Perkin Elmer R32 spectrometers, which operated at 60 and 90 megahertz respectively. Samples were dissolved in deuterated chloroform or acetone with an internal reference, T.M.S.

Microanalysis

The technique described earlier was used to determine the percentage of phosphorus by weight in cold ring fractions and residues.

CHAPTER 3

SYNTHESIS

A SERIES OF POLYURETHANES FROM POLY[BUTYLENE PHENYLPHOSPHONATE]

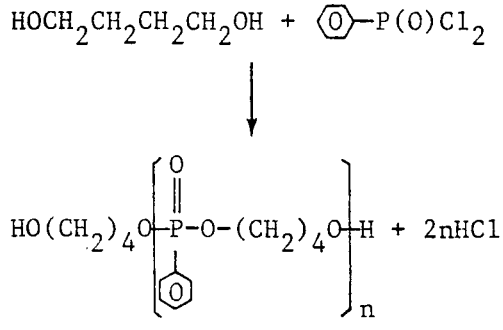
3.1 PURIFICATION OF MONOMERS

1,4-butanediol (B.D.) and methylene bis(4-phenyl isocyanate) (M.B.P.I.) were supplied by B.D.H. Chemical Company. The glycol was distilled twice under vacuum, the middle fraction only being collected. The diisocyanate was distilled once under vacuum then recrystallised from n-hexane[25] . Phenylphosphonodichloridate (P.P.D.) (Aldrich Chemical Company) was distilled under vacuum on two occasions before use.

3.2 PREPARATION OF POLYURETHANE SERIES

Six polyurethanes were prepared using the monomers described. The preparation was designed in three stages which are summarised by the following scheme.

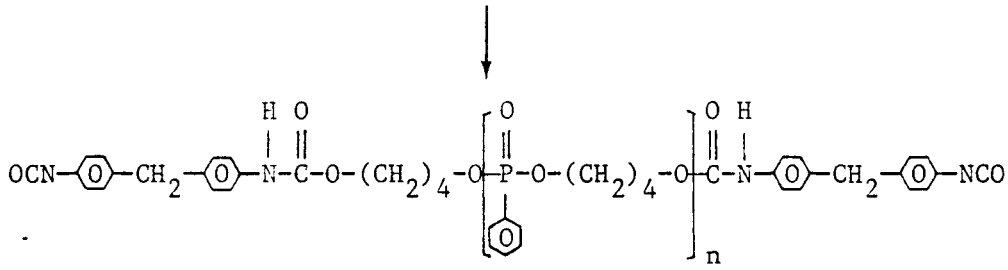
1. Formation of a phosphorus containing polyol by reaction of B.D. with P.P.D.,



(Polyol)

2. Endcapping of the polyol with M.B.P.I. to form prepolymer,

Polyol + 2 M.B.P.I.



(Prepolymer)

3. Preparation of polymers with a range of phosphorus:urethane ratios by reaction of prepolymer, M.B.P.I. and B.D. in various proportions.

These three steps will be discussed in more detail.

Preparation of Poly[butylene phenylphosphonate]

Comparable syntheses have previously been described[26-29] but under a variety of conditions. To carry out the polycondensation in chloroform solution at a temperature near 10° was a compromise between yield and discolouration of products. Several methods to remove the hydrogen chloride which is almost totally retained in the polyol have been reported[26-29]. In addition to those, various ion-exchange resins were tested for effectiveness.

Washing the chloroform solution with an aqueous solution of NaOH, as described by Datskevich[30], was found to be most efficient and convenient.

The entire preparation was carried out as follows.

A solution of 133ml (1.5 mole) B.D. in 150ml dry chloroform was placed in a 2l flask equipped with dropping funnel, stirrer and nitrogen inlet. A water bath maintained the contents at 10° while the system was continuously flushed with dry nitrogen. A solution of 200ml (1.4 mole) P.P.D. in 200ml dry chloroform was added dropwise over a period of 1.5-2 hours with rapid stirring. After stirring the mixture for a further 30 minutes the HCl produced was neutralised by washing the solution with aqueous NaOH. After separation, the polyol, poly[butylene phenylphosphonate] was precipitated from solution by diethylether (1l), collected and redissolved in 1l of chloroform. Diethylether (200ml) was added to precipitate fractions of higher molecular weight and anhydrous $MgSO_4$ to remove moisture. The mixture was then filtered and the solvent removed under reduced pressure by

rotary evaporation.

The polymerisation conditions together with molecular weights and results of microanalysis are given in Table 3.i. N.M.R. and infrared spectra are shown in Figure 3.I.

Preparation of Prepolymer

The conversion of an organic polyester or polyether to a macrodiisocyanate prepolymer before incorporation into a polyurethane structure is a widely used and reported step[18,31–36]. However it has been less frequently applied to polyesters containing phosphorus. Thus experimental conditions of the more common endcapping reactions were considered before arriving at the following procedure.

An appropriate amount of M.B.P.I. was placed in a flask equipped with stirrer and N_2 inlet. Under a continuous flow of nitrogen, the M.B.P.I. was heated to 80^{o} with vigorous stirring and half the molar quantity of polyol added slowly. The temperature was raised to 110^{o} over 20 minutes and the product finally cooled to ambient temperature, forming a colourless, opaque solid.

Confirmation of Reaction

Several tests were conducted to ascertain the product of endcapping had the anticipated prepolymer structure. It seems appropriate to list results here, since they formed part of the synthesis programme.

1. The infrared spectrum of the product shows major absorptions at 3260 cm^{-1} (N-H), 2260 cm^{-1} (N = C = O), 1725 cm^{-1} (amide I) and 1540 cm^{-1} (amide II) thus confirming the formation of urethane links.
2. With a molar ratio M.B.P.I.: polyol = 2, analysis of the free isocyanate content indicated that 50% of isocyanate groups had reacted.
3. A model compound, di-n-butylphenylphosphonate was synthesised[37] and heated with two molar proportions of M.B.P.I. under endcapping conditions. The fact that no reaction was detected suggests that M.B.P.I. reacts exclusively with the terminal -OH groups of the polyol.
4. Thin layer chromatography demonstrated qualitatively that small amounts of unreacted M.B.P.I. were present in the prepolymer, suggesting small amounts of longer chain prepolymer molecules were formed by reaction of both isocyanate functions of some M.B.P.I. molecules.

Table 3.i: Polycondensation to Poly[butylene phenylphosphonate]

Monomer	Concentration, mol l^{-1}	Solvent	Temperature, ^{o}C	Duration, hours	Atmosphere	%P by weight	Molecular Weight	
							V.P.O.	E.G.A.
B.D.	3.3	$CHCl_3$	10	2.5	N_2	11.47	580	1036
P.P.D.	3.1							

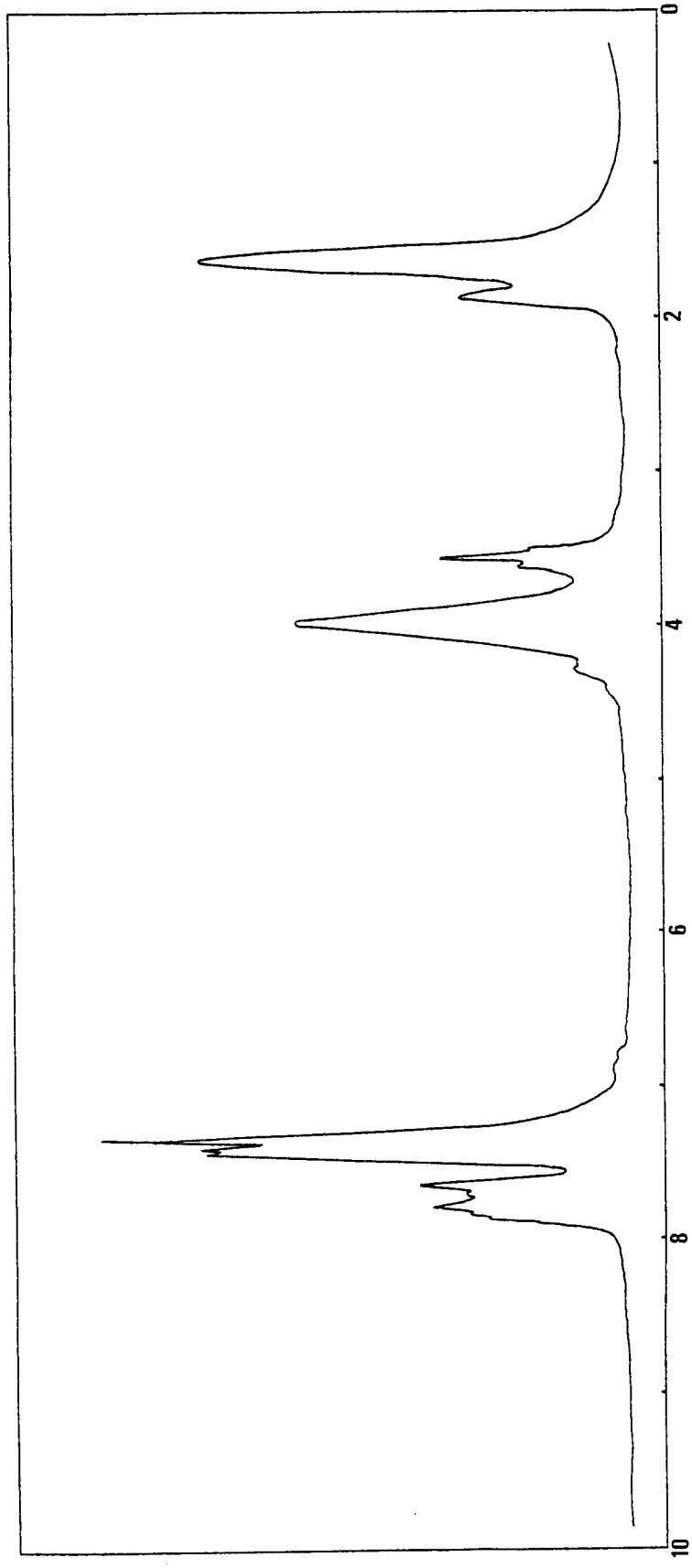


Figure 3.I(a): N.M.R. Spectrum of Poly[butylene phenylphosphonate]

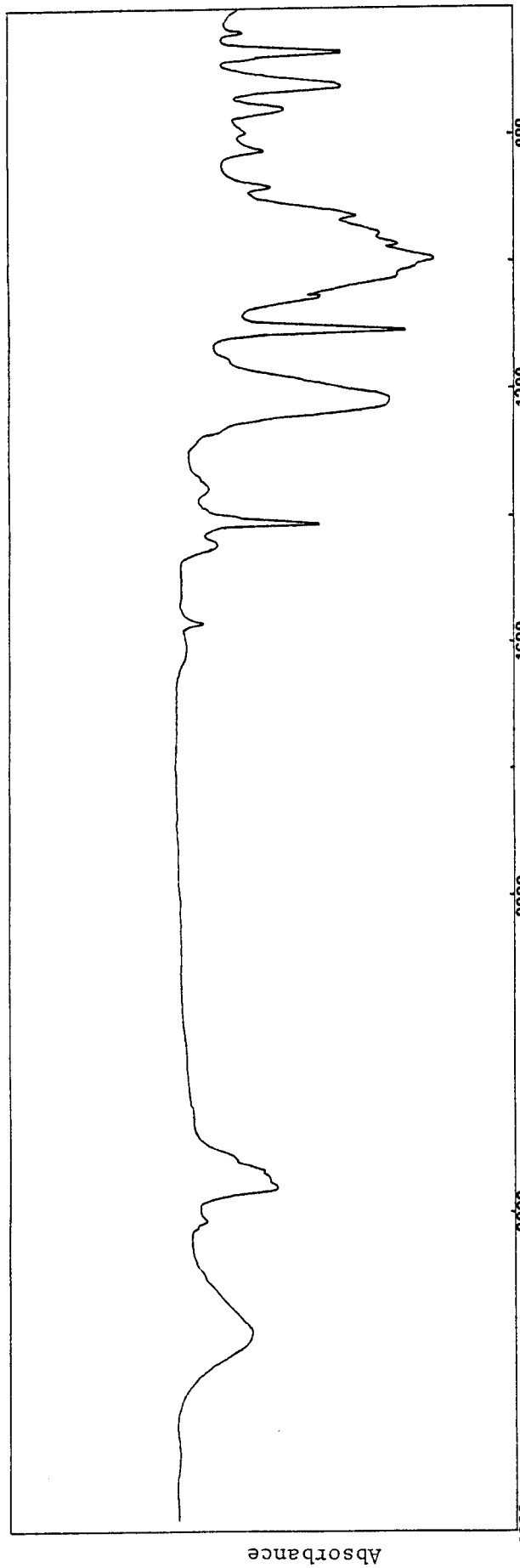


Figure 3.I(b): Infrared Spectrum of Poly[butylene phenylphosphonate]

5. During the reaction traces of gases were sometimes liberated and were identified as CO_2 and tetrahydrofuran, T.H.F. The CO_2 could be formed in three ways.

First, water present as impurity could react with isocyanate groups to give urea and CO_2.

Second, pairs of isocyanate groups could react to form carbodiimide and CO_2.

Third, pairs of hydroxyl groups in the polyol could condense to form water which would lead to CO_2 as before.

The reagents used in the preparation of the prepolymer were all carefully dried and carbodiimide should only form at very much higher temperatures[16]. The third alternative was supported by previous work[38] and further E.G.A. studies confirmed that the molecular weight of the polyol tends to increase slowly on prolonged heating at 110°. This effect would obviously accompany the condensation process suggested.

T.H.F. must result from trace decomposition of the polyol[16].

From this evidence it is reasonable to conclude that the reaction product is predominantly the expected prepolymer, with small amounts of longer chain material of similar structure and only insignificant traces of other products.

Preparation of Polymers

Various reported preparations of polyurethanes[18,35,39-44] were used as a guide to the preparation of the present series of polymers.

Known weights of recrystallised M.B.P.I. and freshly prepared prepolymer were dissolved in sufficient dimethylacetamide (D.M.A.) to form a 1:1 w/v solution. The mixture, in a flask equipped with stirrer, N_2 inlet and reflux condenser with dry outlet was heated to 110° and a 1:1 v/v solution of the appropriate amount of chain extender, B.D. in D.M.A. added. The temperature was maintained between 110 and 115° with rapid stirring for 80 minutes. The polymer (average yield 86%) was precipitated by distilled water, redissolved in dimethylformamide (D.M.F.) and reprecipitated into a large volume of water. Precipitated polymer was filtered, washed with distilled water and acetone, ground to a powder under methanol and dried in a vacuum oven at 40°.

The reaction conditions and range of monomer concentrations are shown in Table 3.ii.

Table 3.ii: Polymerisation to Polyurethane Series

Reagent	Concentration, mol l^{-1}	Solvent, ml	Temperature, ^{o}C	Duration, hours	Atmosphere	Catalyst
Prepolymer	0.10-0.67					
M.B.P.I.	0.008-1.88	D.M.A., 12	115	1, 20	N_2	None
B.D.	0.67-1.99					

POLYURETHANE FROM POLY[BUTYLENE PHENYLPHOSPHATE]

3.3 PURIFICATION OF MONOMERS

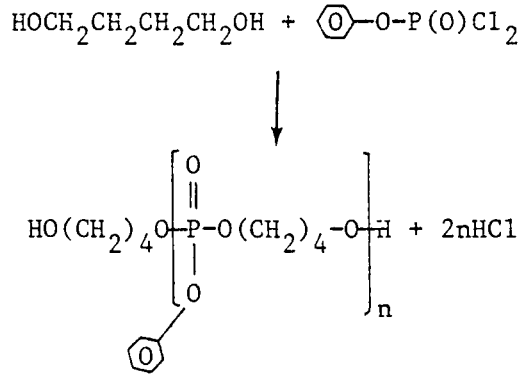
Phenylphosphorodichloridate (P.R.D.) obtained from the Aldrich Chemical Company was distilled twice under reduced pressure. Only the middle fraction was retained. 1,4-butanediol and methylene bis(4-phenyl isocyanate) were purified as before.

3.4 PREPARATION OF POLYURETHANE

The same synthetic route was followed to prepare a polyurethane containing phosphorus in a higher oxidation state.

Preparation of Poly[butylene phenylphosphate]

Butanediol and phenylphosphorodichloridate reacted to form polyol according to the following scheme.



(Polyol)

The product was collected and purified by the method described. The polymerisation conditions together with molecular weights and results of microanalysis are given in Table 3.iii. N.M.R. and infrared spectra are shown in Figure 3.II.

Preparation of Prepolymer

As a result of its molecular weight, the polyol was a waxy solid (m.p. 56°). To mix efficiently with M.B.P.I. during endcapping the polyol was dissolved in a few ml of D.M.A. Stirring was maintained under a continuous flow of nitrogen. The temperature was kept at 90° for one hour and the reaction monitored at regular intervals by infrared spectroscopy.

Table 3.iii: Polycondensation to Poly[butylene phenylphosphate]

Monomer	Concentration, mol l^{-1}	Solvent	Temperature, ^{o}C	Duration, hours	Atmosphere	%P by weight	Molecular Weight	
							V.P.O.	E.G.A.
B.D.	4.3	Chloroform	8-10	3	N_2	12.85	2800	5800
P.R.D.	3.7							

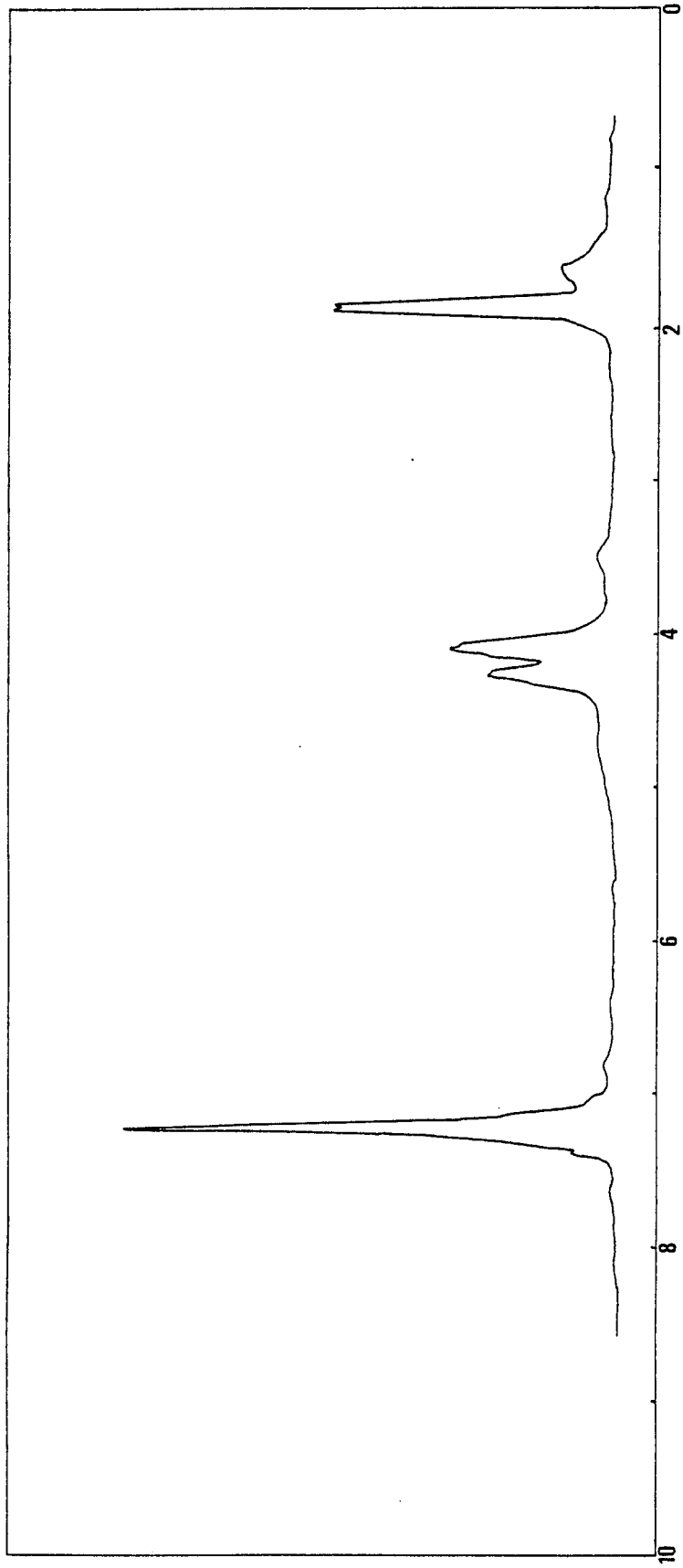


Figure 3.II(a): N.M.R. Spectrum of Poly[butylene phenylphosphate]

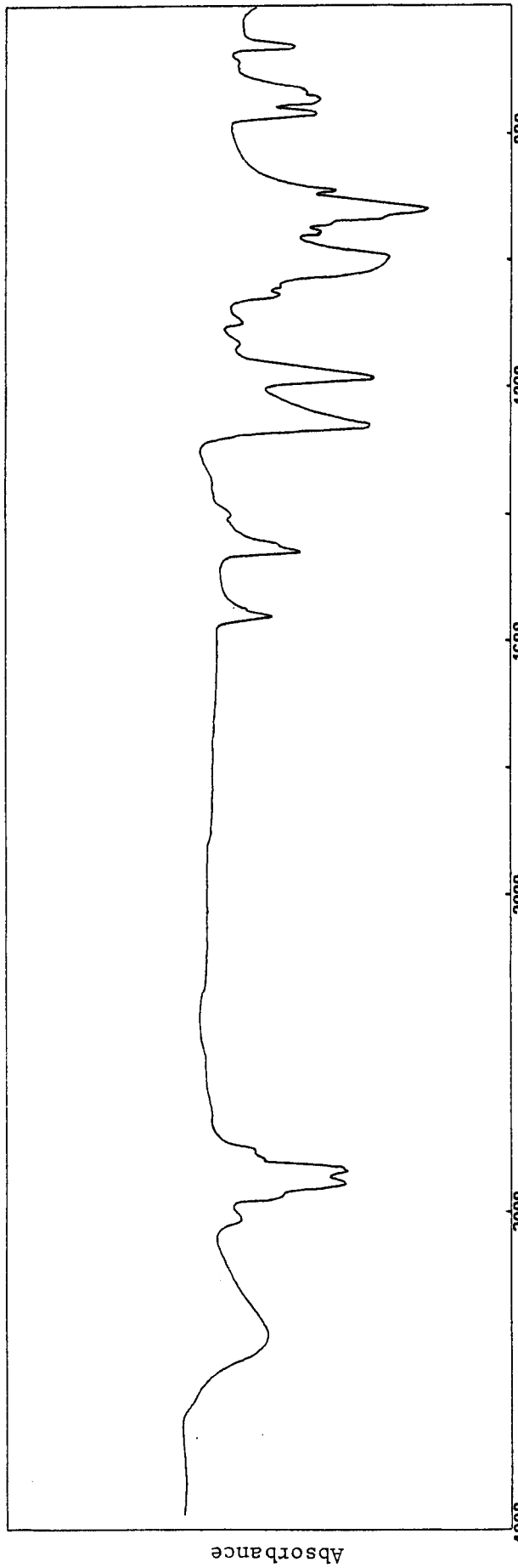


Figure 3.II(b): Infrared Spectrum of Poly[butylene phenylphosphate]

Preparation of Polymer

Experimental conditions similar to those in Table 3.ii were chosen. The proportions of B.D., M.B.P.I. and prepolymer were calculated to produce a polyurethane containing approximately 4% phosphorus by weight. The polymer was precipitated and purified by the usual method. Reaction conditions are reported in Table 3.iv.

Table 3.iv: Polymerisation to Polyurethane from Poly[butylene phenylphosphate]

Reagent	Concentration, mol l^{-1}	Solvent, ml	Temperature, ^{o}C	Duration, hours	Atmosphere	Catalyst
Prepolymer	0.067					
M.B.P.I.	1.81	D.M.A., 18	110	1, 30	N_2	None
B.D.	1.87					

POLYURETHANE FROM POLY[OXYDIETHYLENE PHENYLPHOSPHONATE]

3.5 PURIFICATION OF MONOMERS

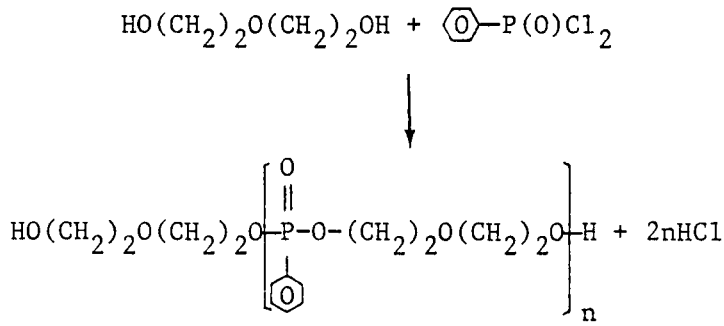
1,4-butanediol and phenylphosphonodichloridate were distilled twice as described earlier. Methylene bis(4-phenyl isocyanate) was purified as before. Diethylene glycol (D.E.G.) (Polysciences) was distilled twice under reduced pressure and the early and late fractions discarded.

3.6 PREPARATION OF POLYURETHANE

Some modifications to the reaction conditions were made and will be described.

Preparation of Poly[oxydiethylene phenylphosphonate]

D.E.G. and P.P.D. reacted to form polyol according to the following scheme.



(Polyol)

The final 30 minutes of polycondensation were carried out at 50°. The work up and purification of the polyol was as before except for removal of high molecular weight fractions. Thus diethyl ether was not added to polyol solution before drying over $MgSO_4$.

The conditions of polycondensation to polyol are given in Table 3.v. The infrared and N.M.R. spectra are shown in Figure 3.III.

Preparation of Prepolymer

The polyol was a viscous liquid which allowed endcapping to be carried out in bulk. Infrared analysis confirmed reaction was complete after stirring for 70 minutes at 75°.

Table 3.v: Polycondensation to Poly[oxydiethylene phenylphosphonate]

Monomer	Concentration, mol l^{-1}	Solvent	Temperature, ^{o}C	Duration, hours	Atmosphere	%P by weight	Molecular Weight	
							V.P.O.	E.G.A.
D.E.G.	8.12	Chloroform	20-50	1	Air	11.95	2172	3978
P.P.D.	8.12							

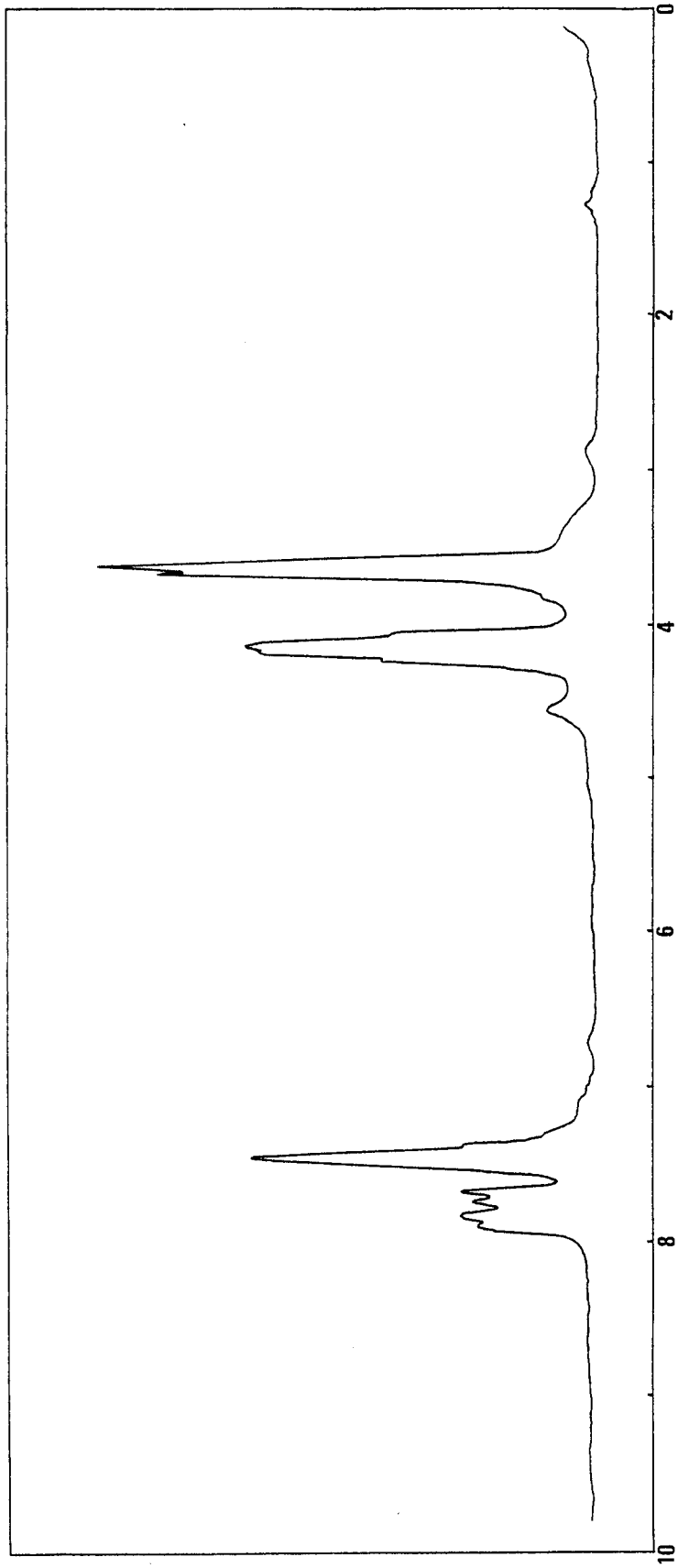


Figure 3.III(a): N.M.R. Spectrum of Poly[oxydiethylene phenylphosphonate]

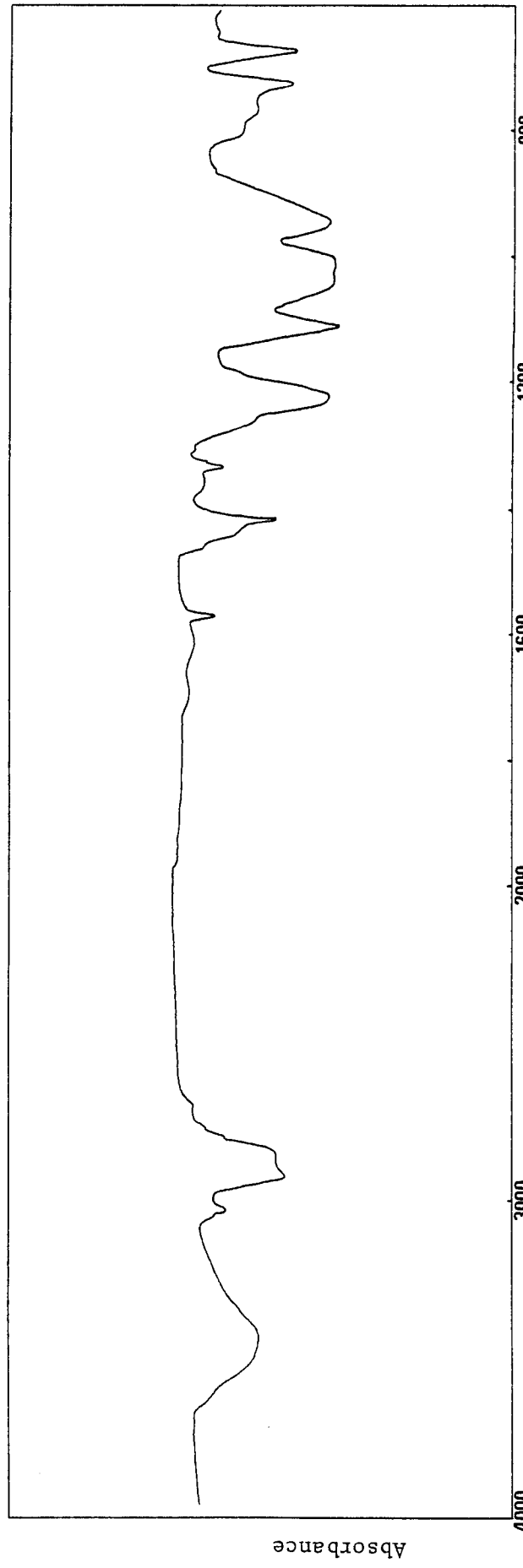


Figure 3.III(b): Infrared Spectrum of Poly[oxydiethylene phenylphosphonate]

Preparation of Polymer

The polymerisation was carried out under similar circumstances as before but in presence of a catalyst. Stannous-2-ethyl hexanoate[45] was mixed with a solution of B.D. in D.M.F. to be added simultaneously to the reaction mixture. The catalyst (0.5% based on total weight of reactants) increased the rate of polymerisation until high molecular weight fractions began to precipitate from solution. At this point reaction was stopped by addition to excess distilled water. The polymer was kept in refluxing methanol overnight and ground under cold methanol to a powder. Samples were dried under vacuum at 70° for several days.

Details of polymerisation are given in Table 3.vi.

Table 3.vi: Polymerisation to Polyurethane from Poly[oxydiethylene phenylphosphonate]

Reagent	Concentration, mol l^{-1}	Solvent, ml	Temperature, ^{o}C	Duration, hours	Catalyst	Concentration, mol l^{-1}
Prepolymer	0.068	D.M.F., 30	110	0, 05	Stannous-2-ethyl hexanoate	0.0108
M.B.P.I.	1.621					
B.D.	1.686					

POLYURETHANE FROM POLY[(ETHYLENE BIS(OXY))DIETHYLENE PHENYLPHOSPHONATE]

3.7 PURIFICATION OF MONOMERS

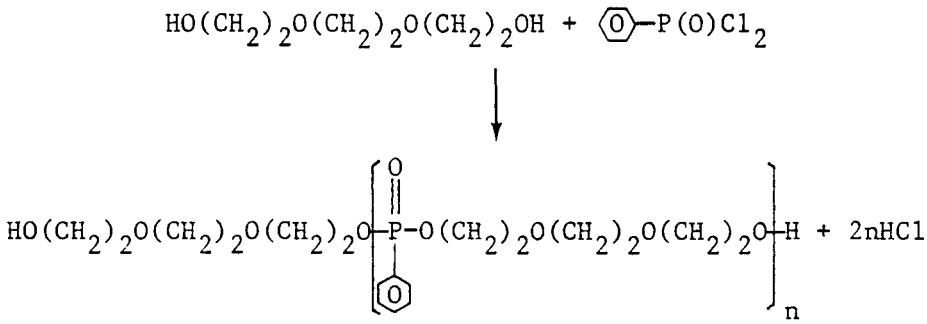
Triethylene glycol (T.E.G.) from Hopkin and Williams Limited was distilled twice under reduced pressure and the middle fraction retained for use. The usual phosphorus compound P.P.D., diisocyanate M.B.P.I. and chain extender B.D. were purified.

3.8 PREPARATION OF POLYURETHANE

The same approach was repeated to prepare the final polyurethane. In the final stage sufficient prepolymer was used to produce polyurethane containing approximately 4% phosphorus by weight. Details of the three steps are given.

Preparation of Poly[(ethylene bis(oxy))diethylene phenylphosphonate]

T.E.G. and P.P.D. reacted in solution to form polyol according to the scheme,



(Polyol)

A slightly higher temperature of 50° was maintained during the second half of polycondensation. High molecular weight fractions were not removed from polyol solution before drying and evaporation of solvent.

Details of this step are given in Table 3.vii. N.M.R. and infrared spectra of the polyol are shown in Figure 3.IV.

Preparation of Prepolymer

Endcapping the polyol was performed in bulk with rapid stirring at 74°. The reaction, complete after one hour, was monitored by infrared analysis of aliquots taken at regular intervals.

Table 3.vii: Polycondensation to Poly[(ethylene bis(oxy))diethylene phenylphosphonate]

Monomer	Concentration, mol l^{-1}	Solvent	Temperature, ^{o}C	Duration, hours	Atmosphere	%P by weight	Molecular Weight	
							V.P.O.	E.G.A.
T.E.G.	8.83	Chloroform	20-50	1	Air	10.18	1560	2116
P.P.D.	8.80							

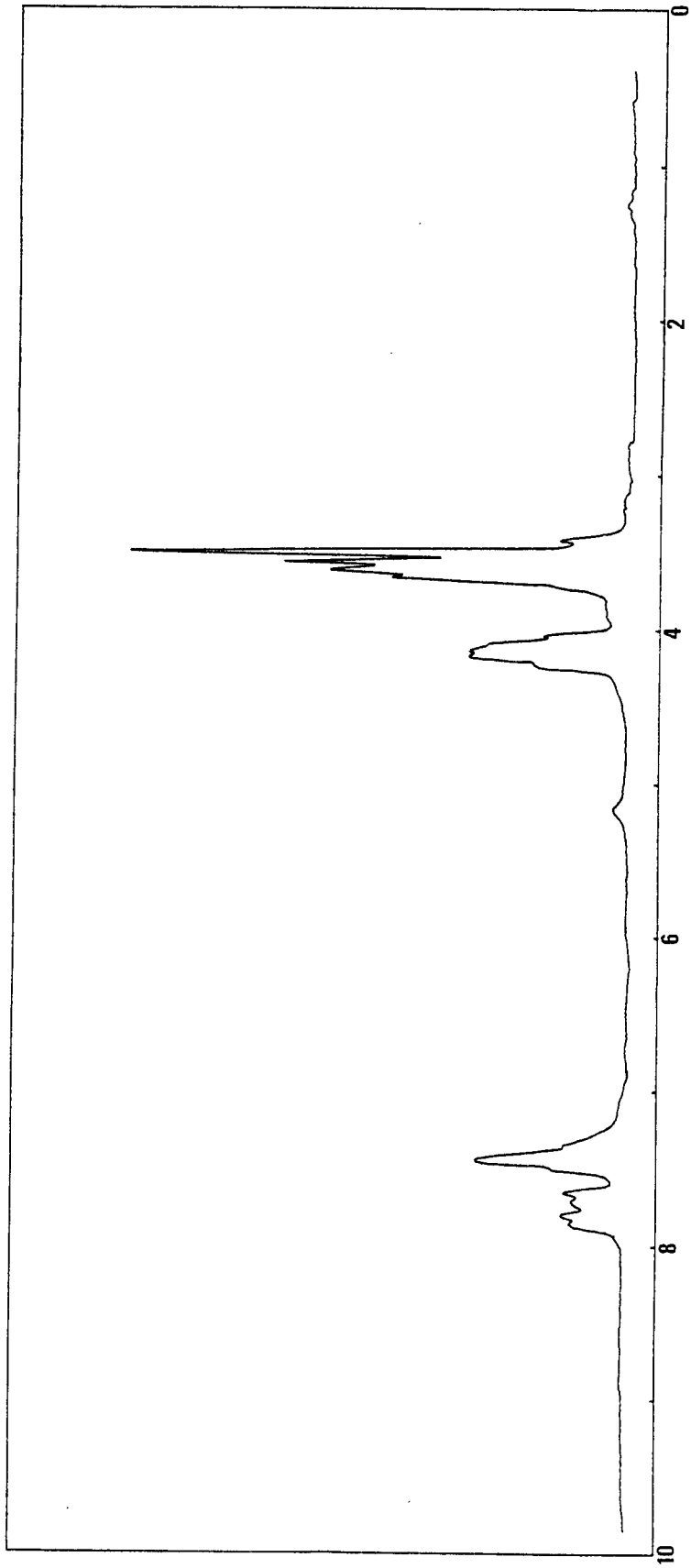


Figure 3.IV(a): N.M.R. Spectrum of Poly[(ethylene bis(oxy))diethylene phenylphosphonate]

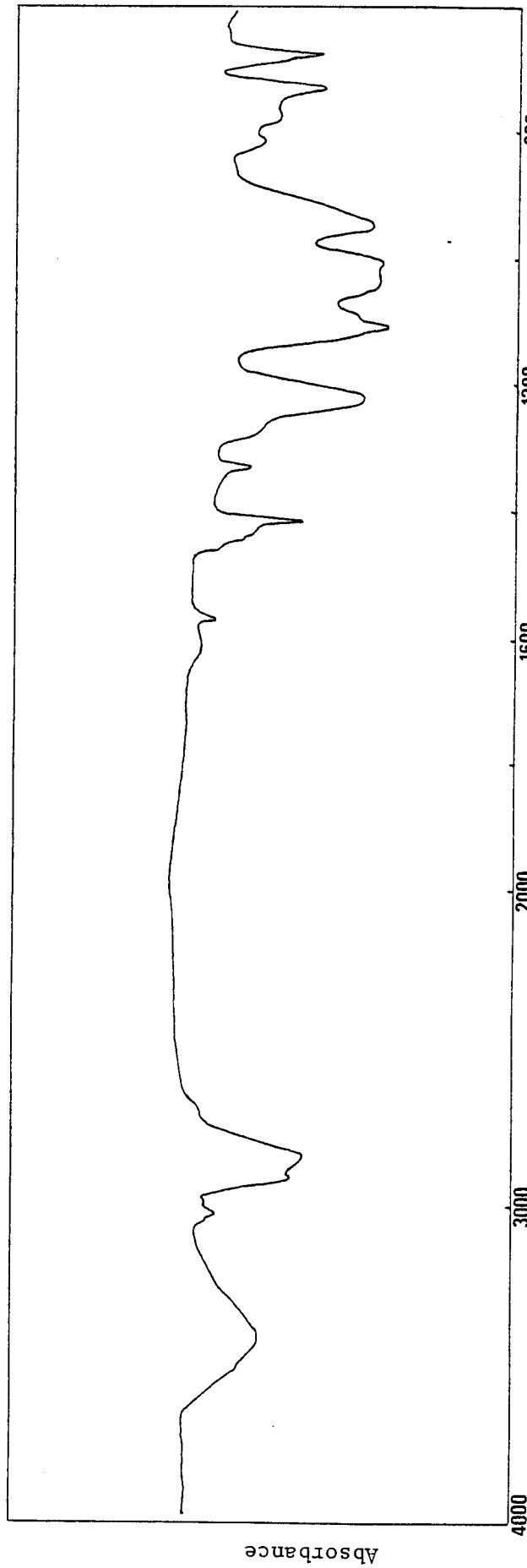


Figure 3.IV(b): Infrared Spectrum of Poly[(ethylene bis(oxy))diethylene phenylphosphonate]

Preparation of Polymer

Polymerisation was conducted under the same conditions as in the preceding case (see Table 3.vi). However lower concentrations of reagent and catalyst were chosen to control molecular weight. Polymer was reprecipitated from D.M.F. by distilled water, ground under acetone then methanol and dried under high vacuum at 70^{o} for some days.

The polymerisation is summarised in Table 3.viii.

Table 3.viii: Polymerisation to Polyurethane from Poly[(ethylene bis(oxy))diethylene phenylphosphonate]

Reagent	Concentration, mol l^{-1}	Solvent, ml	Temperature, ^{o}C	Duration, hours	Catalyst	Concentration, mol l^{-1}
Prepolymer	0.076	D.M.F., 50	110-116	1, 10	Stannous-2-ethyl hexanoate	0.0037
M.B.P.I.	0.743					
B.D.	0.820					

CHAPTER 4

NOMENCLATURE AND CHARACTERISATION

4.1 INTRODUCTION

The polyurethanes described in Chapter 3 differ only slightly in structure. In this chapter the formula and symbol of each polymer has been clearly set out and may be referred to during the rest of the report.

Infrared and N.M.R. spectra are presented together with results of microanalysis to characterise the polymers.

4.2 A SERIES OF POLYURETHANES FROM POLY[BUTYLENE PHENYLPHOSPHONATE]

Nomenclature

The series of polyurethanes comprised six polymers prepared as described in Chapter 3, page 35. Each member of the series has been named polyurethane 1, P.U.1. By altering the proportions of prepolymer, M.B.P.I. and B.D. in the final polymerisation different amounts of phosphorus have been incorporated into the backbone chain of each member. A subscript has been used to indicate the theoretical amount of phosphorus present and describes the ratio of moles phosphorus:moles urethane links in the polymer.

Thus the polymer prepared from

0.0039 moles prepolymer,
0.0120 moles M.B.P.I.
and 0.0159 moles B.D.

should contain 0.0174 moles of phosphorus and 0.0396 moles of urethane links. The ratio moles phosphorus : moles urethane links = 0.439 and the polymer designated $P.U.1_{(44)}$.

Structure of Polymers

The structures of the six polyurethanes in this series are illustrated in Figure 4.I. Brackets are drawn for P.U.1$_{(0)}$ and P.U.1$_{(111)}$ when the repeat unit is accurately known. The single formula which shows a random copolymer represents the remaining members of the series, P.U.1$_{(11)}$-P.U.1$_{(54)}$. The wavy line denotes the portion of polymer which was originally prepolymer. Once copolymerised into the backbone of the polyurethane this portion may be referred to as the phosphorus polyester segment.

Characterisation

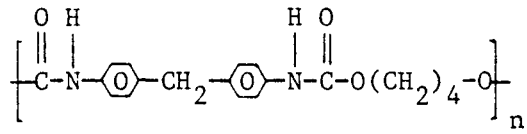
Spectroscopy: The infrared spectrum of P.U.1$_{(0)}$ has been published and assignments made for all absorption bands[16,46]. Since the phosphorus-phenyl bond is characterised by three strong, sharp absorptions occurring at 1440, 1130 and 995 cm^{-1} (see Chapter 3, Figure 3.I) the presence of the phosphorus polyester segment in polyurethane 1 was easily identified by infrared measurements. Similarly the presence of phosphorus was registered by equally distinct absorptions at 750 and 700 cm^{-1} caused by aromatic C-H bend on the phenyl group[47].

Comparison of the infrared spectra of polyurethanes 1 showed the intensity of these bands to increase as expected across the series. The spectra of P.U.1$_{(0)}$, P.U.1$_{(44)}$ and P.U.1$_{(111)}$ are drawn in Figure 4.II. Assignments of major absorptions are recorded in Table 4.i.

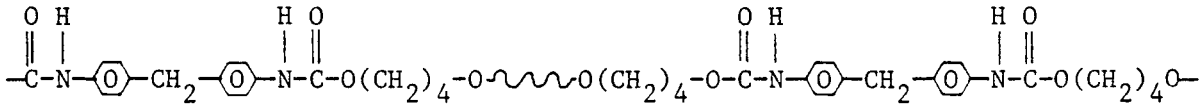
By taking aromatic hydrogen absorption as an indication of phosphorus, proton N.M.R. spectroscopy was used to similar effect. The N.M.R. spectrum of P.U.1$_{(0)}$ shows on AA'BB' quartet (δ = 7.25 p.p.m.) arising from the para-disubstituted phenylene group. A further signal from monosubstituted phenyl ($\delta \cong$ 7.70 p.p.m.) appears in the N.M.R. spectra of subsequent members of the series which contain phosphorus.

^{1}H N.M.R. spectra of P.U.1$_{(0)}$, P.U.1$_{(22)}$ and P.U.1$_{(54)}$ are shown in Figure 4.III. The protons responsible for each signal are listed in Table 4.ii. By comparison with the spectrum of poly[butylene phenyl-phosphonate] (see Chapter 3, Figure 3.I) the presence of the polyester segment in P.U.1$_{(22)}$ and P.U.1$_{(54)}$ becomes clear. The singlet at δ = 9.45 p.p.m. denotes the urethane proton which, because of the polar nature of the solvent, d_6 D.M.S.O. is unaffected by the powerful quadrupole of the nitrogen[48]. Thus integration and the molecular weight of the polyol allow the abundance of phosphorus in each

P.U.I$_{(0)}$



P.U.I$_{(11)}$-P.U.I$_{(54)}$



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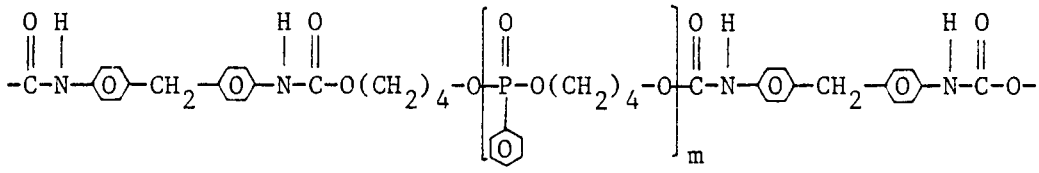
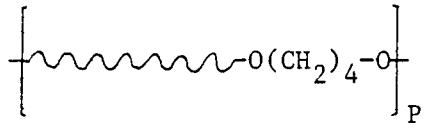
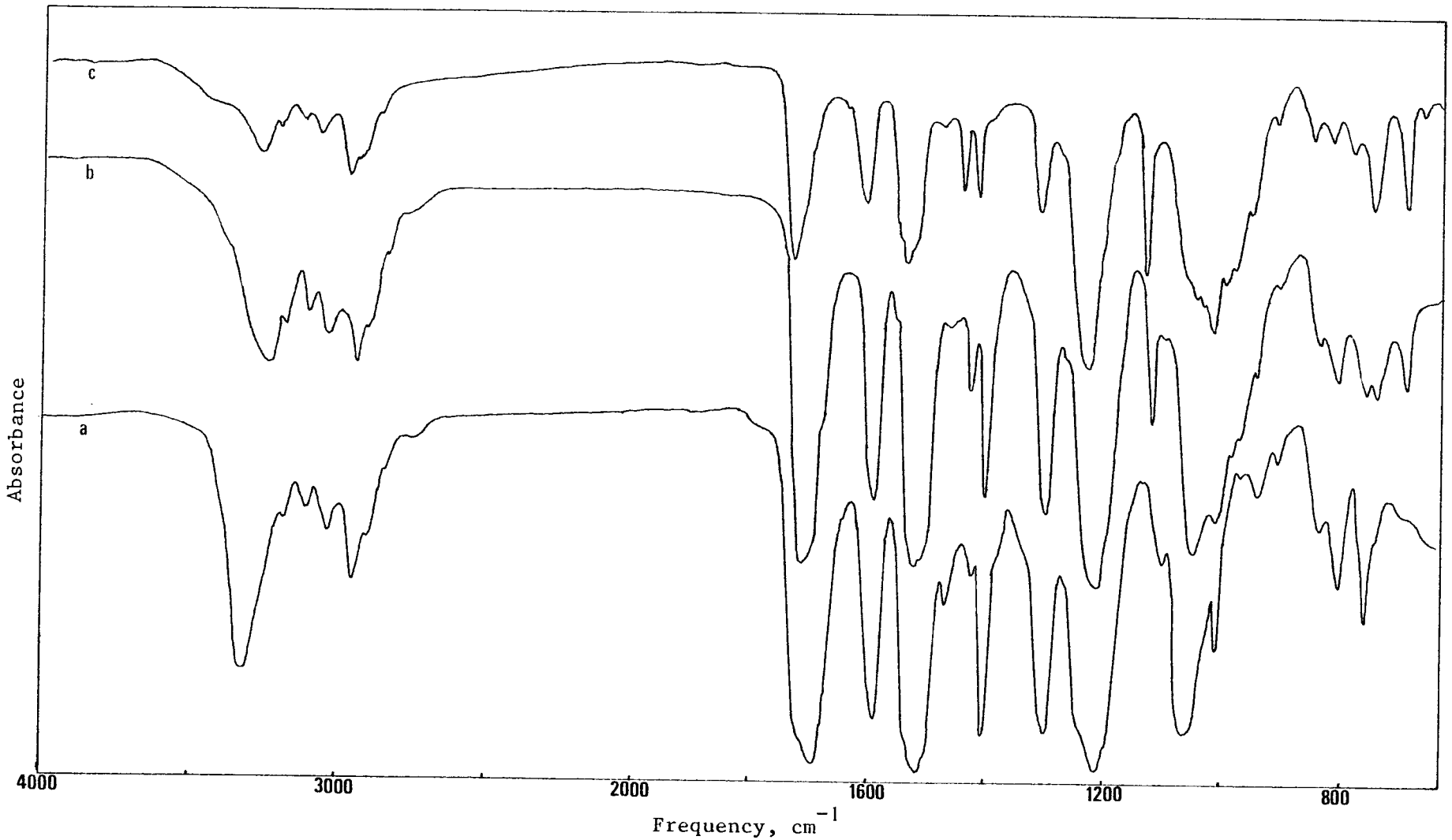


P.U.I$_{(111)}$



where ~~~ is as before

Figure 4.I: Structures of Poly[butylene phenylphosphonate]



I.R. Spectra: a = P.U.I$_{(0)}$, b = P.U.I$_{(44)}$, c = P.U.I$_{(111)}$

Figure 4.II: Infrared Spectra of P.U.I$_{(0)}$, P.U.I$_{(44)}$ and P.U.I$_{(111)}$

Table 4.i

Frequency (cm^{-1})	Relative Intensity*	Assignment**
~3300	(m)	ν N-H
3200	(w)	ν C-H in aromatic rings
3125	(w)	
~3035	(w)	
2960	(m)	ν C-H in aliphatic chain
2900	(sh)	
1740-1690	(s)	ν C = O amide I
1600	(m)	ν C = C in aromatic rings
1550-1500	(s)	amide II
1475	(w)	δ C-H in aliphatic chain
1440	(v)	P—⬡ absorption
1415	(m)	ν C-C in aromatic rings
1310	(m)	β C-H in aromatic rings
1260-1200	(s)	ν CO-O-C amide III ν P = O
1130	(v)	P—⬡ absorption
1075	(m)	ν CO-O-C
1020	(m)	β C-H in aromatic rings
1040-980	(m)	ν P-O
995	(v)	P—⬡ absorption
980	(w)	r C-H in aliphatic chain
950	(w)	
915	(w)	γ C-H in p disub aromatic ring
850	(w)	r C-H in aliphatic chain
820	(w)	γ C-H in p disub aromatic ring
775	(w)	γ C = O
750	(m-w)	γ C-H in monosub aromatic ring
695	(m-w)	

* s = strong, m = medium, w = weak, sh = shoulder, v = variable

** ν = stretching, δ = bending, r = rocking, β = in plane bending, γ = out-of-plane bending

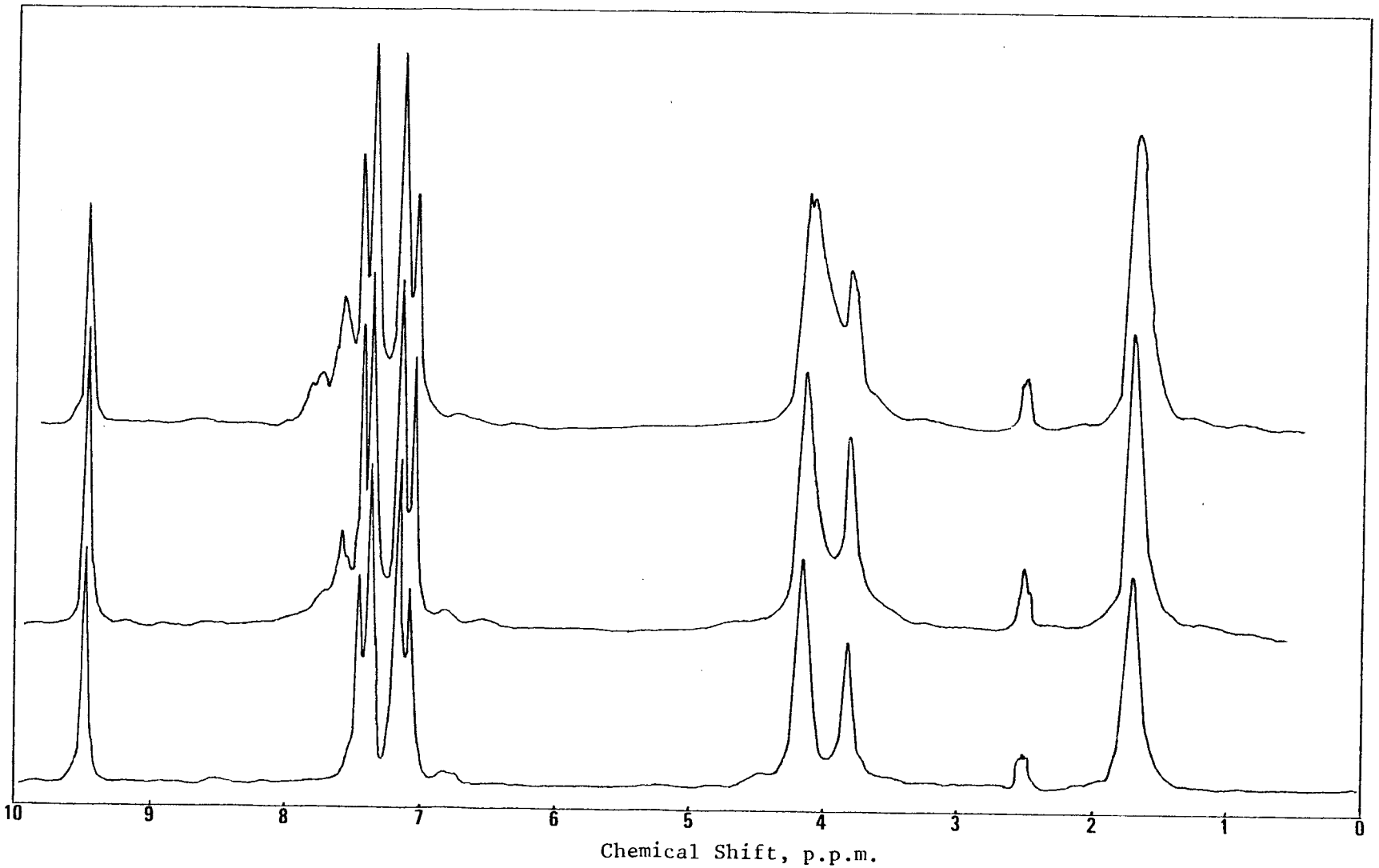
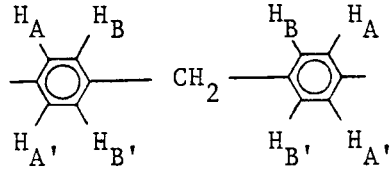


Figure 4.III: N.M.R. Spectra of P.U.1(0), P.U.1(22) and P.U.1(54)

Table 4.ii

Chemical Shift (p.p.m.)	Signal	Assignment
1.70	Broad Singlet	$-OCH_2\underline{CH_2}\underline{CH_2}CH_2O-$ in urethane and polyester segment
3.79	Broad Singlet	$-OOCNH-C_6H_4-\underline{CH_2}-C_6H_4-NHCOO-$
4.11	Broad Singlet	$-O\underline{CH_2}CH_2CH_2\underline{CH_2}O-$ in urethane and polyester segment
7.25	AA'BB' Quartet	
~7.7	Broad Multiplet	$=P-C_6H_5$ aromatic protons
9.45	Sharp Singlet	$-\underline{N}H-C(=O)-O-$

polyurethane to be calculated.

Microanalysis: The phosphorus content obtained by N.M.R. is listed together with abundance of H, C, N and P by microanalysis and molecular weight in Table 4.iii.

4.3 POLYURETHANE FROM POLY[BUTYLENE PHENYLPHOSPHATE]

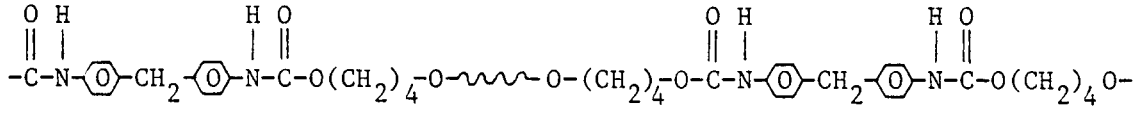
Nomenclature

The second polyurethane, prepared from poly[butylene phenylphosphate] has been designated polyurethane 2. From the molar proportions of prepolymer, M.B.P.I. and B.D. given in Chapter 3, Table 3.iv, the ratio moles phosphorus : moles urethane links is 0.43. The polyurethane therefore has been designated $P.U.2_{(43)}$.

Structure of Polymer

The structure of $P.U.2_{(43)}$ is shown in Figure 4.IV. This is the only polyurethane which we have prepared which contains a polyphosphate segment.

$P.U.2_{(43)}$



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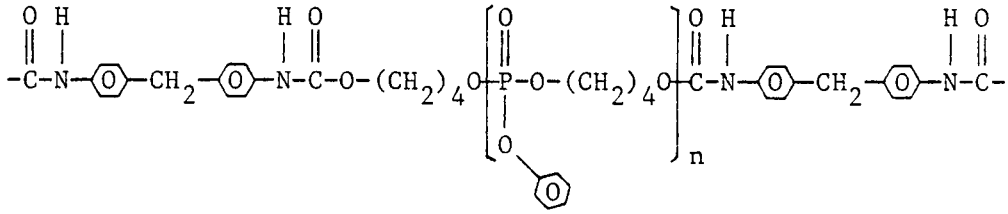


Figure 4.IV

Characterisation

Spectroscopy: The infrared spectrum of the polyurethane is shown in Figure 4.V. Only the absorption at 945 cm^{-1} arising from P-O-Aryl vibrations in the polyester segment does not overlap other parts of the spectrum and indicates the presence of phosphorus. The doublet at 750 and 700 cm^{-1} which is a characteristic of monosubstituted benzene is present but with weak intensity.

However when compared with the infrared spectrum of $P.U.1_{(0)}$ in Figure 4.II the profile and intensity of absorption at 3250 cm^{-1} and

Table 4.iii

Polyurethane	%C Found	%C (Calculated)	%N Found	%N (Calculated)	%H Found	%H (Calculated)	%P By N.M.R.	%P Found	%P (Calculated)	Molecular Weight $\overline{M}_n$
P.U.I$_{(0)}$	66.77	(67.05)	8.24	(8.23)	6.01	(5.88)	0	0	(0)	17 200
P.U.I$_{(11)}$	64.58	(65.80)	7.11	(7.25)	6.14	(5.90)	0.51	1.48	(1.77)	15 600
P.U.I$_{(22)}$	64.38	(64.90)	6.87	(6.54)	5.59	(5.91)	4.43	2.49	(3.07)	14 100
P.U.I$_{(44)}$	63.26	(63.30)	5.94	(5.29)	6.06	(5.96)	4.51	3.74	(5.22)	10 500
P.U.I$_{(54)}$	63.17	(62.95)	5.86	(4.99)	5.70	(5.95)	5.36	3.76	(5.82)	———*
P.U.I$_{(111)}$	60.24	(60.98)	4.02	(3.46)	5.81	(6.02)	8.21	6.36	(8.48)	———*

* P.U.I$_{(54)}$ and P.U.I$_{(111)}$ diffused significantly through the osmometer membrane during measurement. Their molecular weights were clearly less than 10 000(

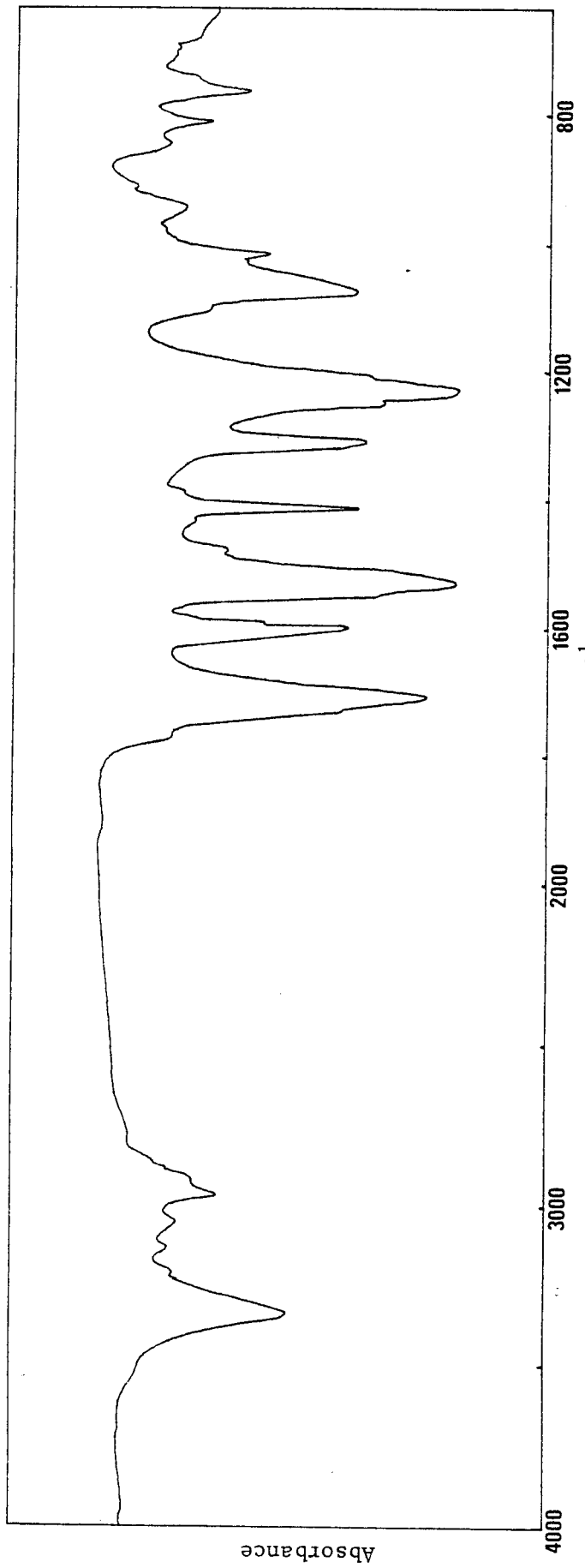


Figure 4.V: Infrared Spectrum of P.U.2(43)

the absorption band in the region 1000-1070 cm^{-1} are clearly different for the two polymers. The infrared spectrum does then show $P.U.2_{(43)}$ contains polyphosphate segments. Assignments of major absorptions are presented in Table 4.iv.

The proton N.M.R. spectrum of $P.U.2_{(43)}$, shown in Figure 4.VI, is very similar to that of $P.U.1_{(22)}$. Integration of the singlet at δ = 9.45 p.p.m. and the aromatic region confirms the success of copolymerisation. Table 4.v gives the chemical shifts of the peaks and the corresponding protons in the polymer.

Microanalysis: The results of microanalysis and phosphorus abundance by N.M.R. integration are given in Table 4.vi. Microanalysis and spectroscopic characterisation of $P.U.2_{(43)}$ compare most closely with these for $P.U.1_{(11)}$ or $P.U.1_{(22)}$ suggesting that the prepolymer of polyurethane 2 did polymerise but not to its full extent.

4.4 POLYURETHANE FROM POLY[OXYDIETHYLENE PHENYLPHOSPHONATE]

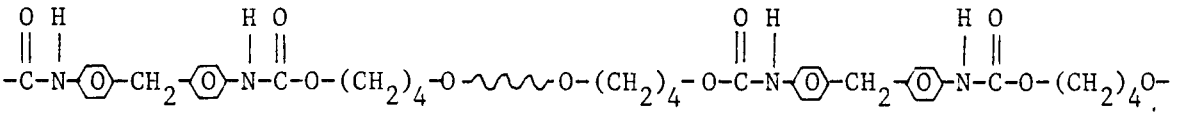
Nomenclature

The third polyurethane to be investigated was polymerised from poly[oxydiethylene phenylphosphonate]. This polymer was prepared to give a theoretical ratio of moles phosphorus : moles urethane links equal to 0.341 and has been named $P.U.3_{(34)}$.

Structure of the Polymer

The structure of $P.U.3_{(34)}$ is drawn in Figure 4.VII. The polyester segment of this polyurethane had the longest chain length of all polyphosphonates prepared. The average number of repeat units in each segment was 17.

$P.U.3_{(34)}$



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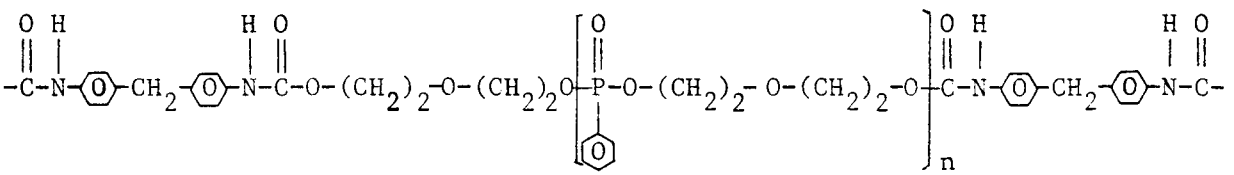


Figure 4.VII

Table 4.iv

Frequency (cm^{-1})	Relative Intensity*	Assignment**
3330	(m)	ν N-H
3200	(w)	ν C-H in aromatic rings
3125	(w)	
3040	(w)	
2960	(w)	ν C-H in aliphatic chain
2900	(sh)	
1740-1680	(s)	ν C = O amide I
1600	(m)	ν C = C in aromatic rings
1550-1500	(s)	amide II
1415	(m)	ν C-C in aromatic rings
1310	(m)	β C-H in aromatic rings
1230	(s)	ν CO-O-C amide III and ν P = O
1075	(m)	ν CO-O-C
1020	(m)	β C-H in aromatic rings
945	(m)	ν P-O-(-Ar)
810	(w)	γ C-H in p-disub aromatic ring
765	(w)	γ C = O
750	(sh)	γ C-H in monosub aromatic ring
695	(sh)	

* s = strong, m = medium, w = weak, sh = shoulder

** ν = stretching, δ = bending, r = rocking, β = in-plane bending, γ = out-of-plane bending

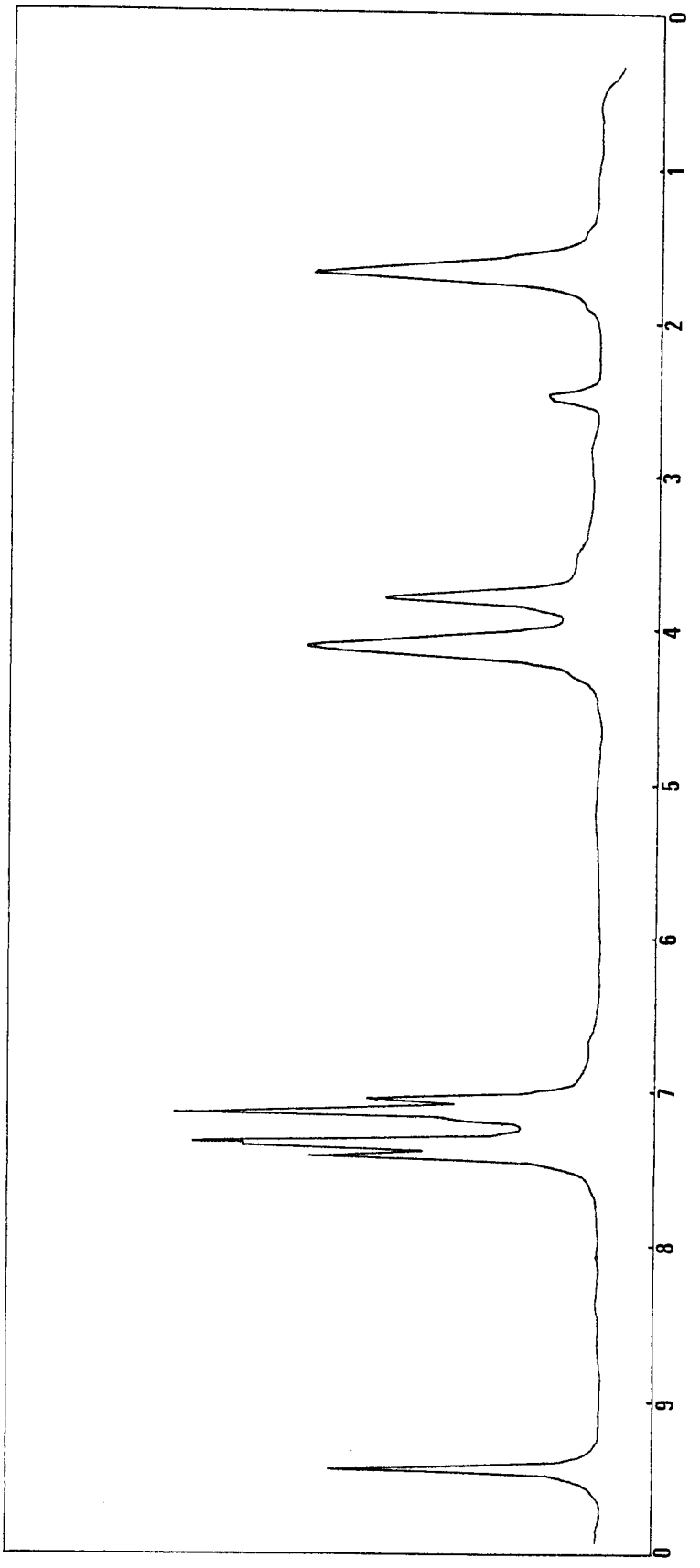


Figure 4.VI: N.M.R. Spectrum of P.U.2(43)

Table 4.v

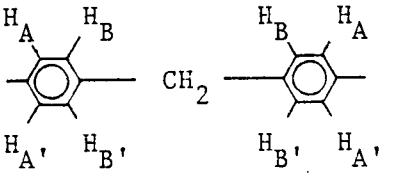
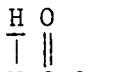
Chemical Shift (p.p.m.)	Signal	Assignment
1.70	Broad Singlet	$-OCH_2\underline{CH_2}\underline{CH_2}CH_2O-$ in urethane and polyester segment
3.79	Broad Singlet	$-OOCNH-C_6H_3-\underline{CH_2}-C_6H_3-NHCOO-$
4.11	Broad Singlet	$-OCH_2CH_2CH_2\underline{CH_2}O-$ in urethane and polyester segment
7.25	AA'BB' Quartet	
7.35	Shoulder	$-P-O-C_6H_5$ aromatic protons
9.45	Sharp Singlet	

Table 4.vi

Polyurethane	%C Found (Calculated)	%N Found (Calculated)	%H Found (Calculated)	%P By N.M.R. Found (Calculated)
P.U.2$_{(43)}$	65.77 (61.61)	8.02 (5.26)	5.97 (5.80)	3.05 2.36 (4.93)

Characterisation

Spectroscopy: The infrared spectrum of $P.U.3_{(34)}$, shown in Figure 4.VIII, was found to contain all absorptions characteristic of polyurethane. The spectrum also highlighted the presence of polyester by the familiar phosphorus-phenyl absorptions and the absorption at 970 cm^{-1} (see Chapter 3, Figure 3.III). As before bands at 750 and 700 cm^{-1} inferred the presence of phosphorus. Assignments of major absorptions are given in Table 4.vii[49,50].

Polyurethane 3 was not sufficiently soluble in dimethylsulphoxide to record nuclear magnetic resonance spectra.

Microanalysis: The results of microanalysis are given in Table 4.viii.

4.5 POLYURETHANE FROM POLY[(ETHYLENE BIS(OXY))DIETHYLENE PHENYLPHOSPHONATE]

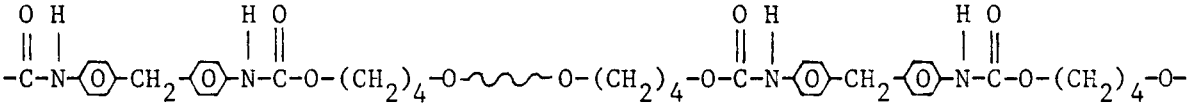
Nomenclature

The final polyurethane, prepared from poly[(ethylene bis(oxy))-diethylene phenylphosphonate], was designated polyurethane 4. The mole ratio phosphorus : urethane = 0.310 was calculated from the quantities of prepolymer, M.B.P.I. and B.D. used for polymerisation (see Chapter 3, Table 3.viii). The abbreviation $P.U.4_{(31)}$ was chosen for the polyurethane.

Structure of the Polymer

The structure of polyurethane 4 is illustrated in Figure 4.IX. The average number of repeat units in the phosphorus polyester segment was calculated to be 7.

$P.U.4_{(31)}$



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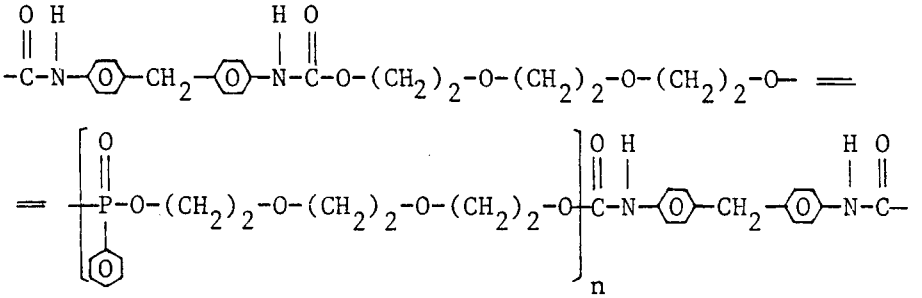


Figure 4.IX

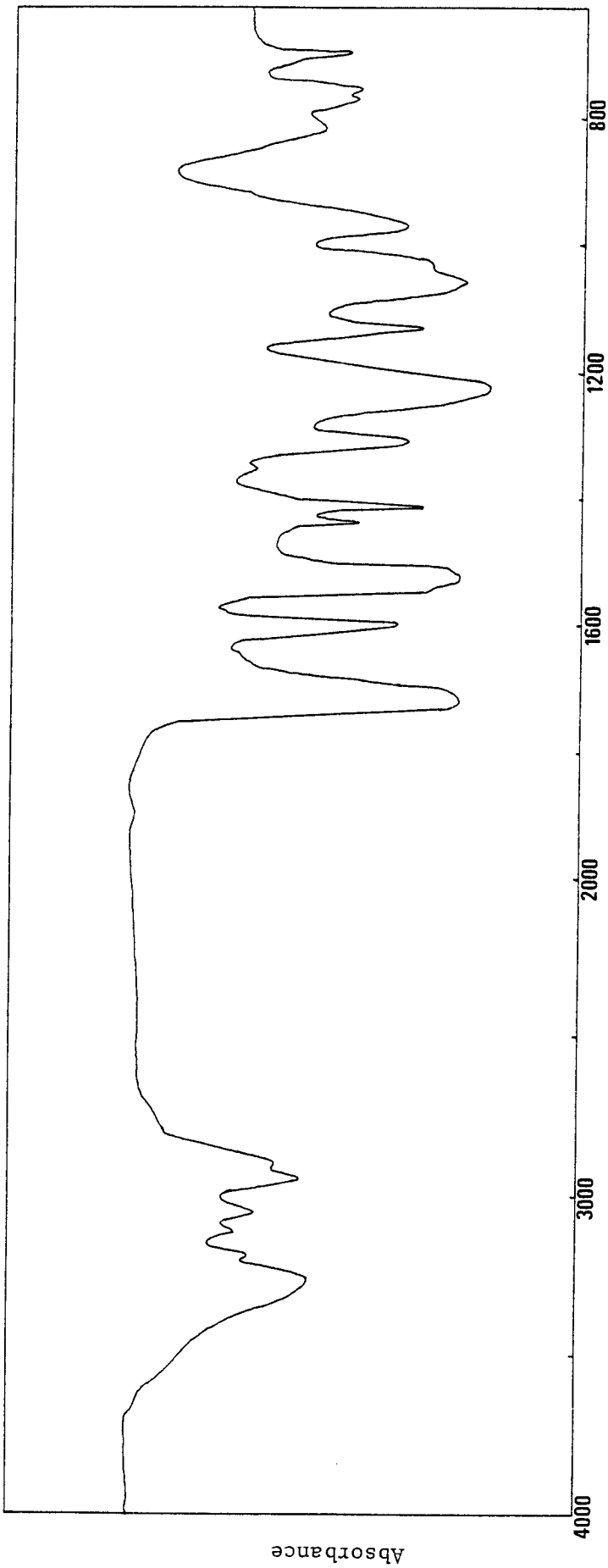


Figure 4.VIII: Infrared Spectrum of P.U.3 (34)

Table 4.vii

Frequency (cm^{-1})	Relative Intensity*	Assignment**
~3300	(m)	ν N-H
3200	(w)	ν C-H in aromatic rings
3125	(w)	
3050	(w)	
2965	(w)	ν C-H in aliphatic chain
2900	(w)	
2880	(sh)	
1740-1680	(s)	ν C = O amide I
1600	(m)	ν C = C in aromatic rings
1550-1500	(s)	amide II
1435	(w)	δ C-H in aliphatic chain
1415	(m)	ν C-C in aromatic rings
1352	(w)	w C-H in aliphatic chain
1310	(m)	β C-H in aromatic rings
1270-1200	(s)	ν CO-O-C amide III and ν P = O
1130	(m)	P-⟨O⟩ absorption and ν C-O-C
1070	(m)	ν CO-O-C
1020	(sh)	β C-H in aromatic rings
970	(m)	r C-H in aliphatic chain
850	(sh)	r C-H in aliphatic chain
815	(w)	γ C-H in p-disub aromatic ring
770	(w)	γ C = O
750	(w)	γ C-H in monosub aromatic ring
695	(w)	

* s = strong, m = medium, w = weak, sh = shoulder

** ν = stretching, w = wagging, r = rocking, β = in-plane bending, γ = out-of-plane bending

Table 4.viii

Polyurethane	%C Found (Calculated)	%N Found (Calculated)	%H Found (Calculated)	%P Found (Calculated)
P.U.3 (34)	62.35 (62.44)	6.09 (5.64)	5.99 (5.83)	3.72 (4.25)

Characterisation

Spectroscopy: The infrared spectrum of P.U.$4_{(31)}$, shown in Figure 4.X, is similar to that of P.U.$3_{(34)}$. The spectrum of the polyester urethane includes the characteristic absorptions of phosphorus-phenyl and monosubstituted benzene segments. It clearly indicates the copolymerised phosphorus. Assignments of absorptions are identical to those in Table 4.vii.

Relative absorption intensities in the spectra of P.U.$3_{(34)}$ and P.U.$4_{(31)}$ suggests that the concentration of phosphorus is lower than anticipated. This was confirmed by microanalysis.

Proton N.M.R. of polyurethane 4 was recorded. As before the technique allowed an estimation of the abundance of phosphorus using integration values and the chain length of the polyester segment. The N.M.R. spectrum is illustrated in Figure 4.XI and assignments stated in Table 4.ix.

Microanalysis: Table 4.x lists the abundance of phosphorus obtained by N.M.R. and by microanalysis. In all the polyurethanes prepared, the percentage of phosphorus determined by microanalysis was less than the theoretical amount. This feature is consistent with other reports[40,43].

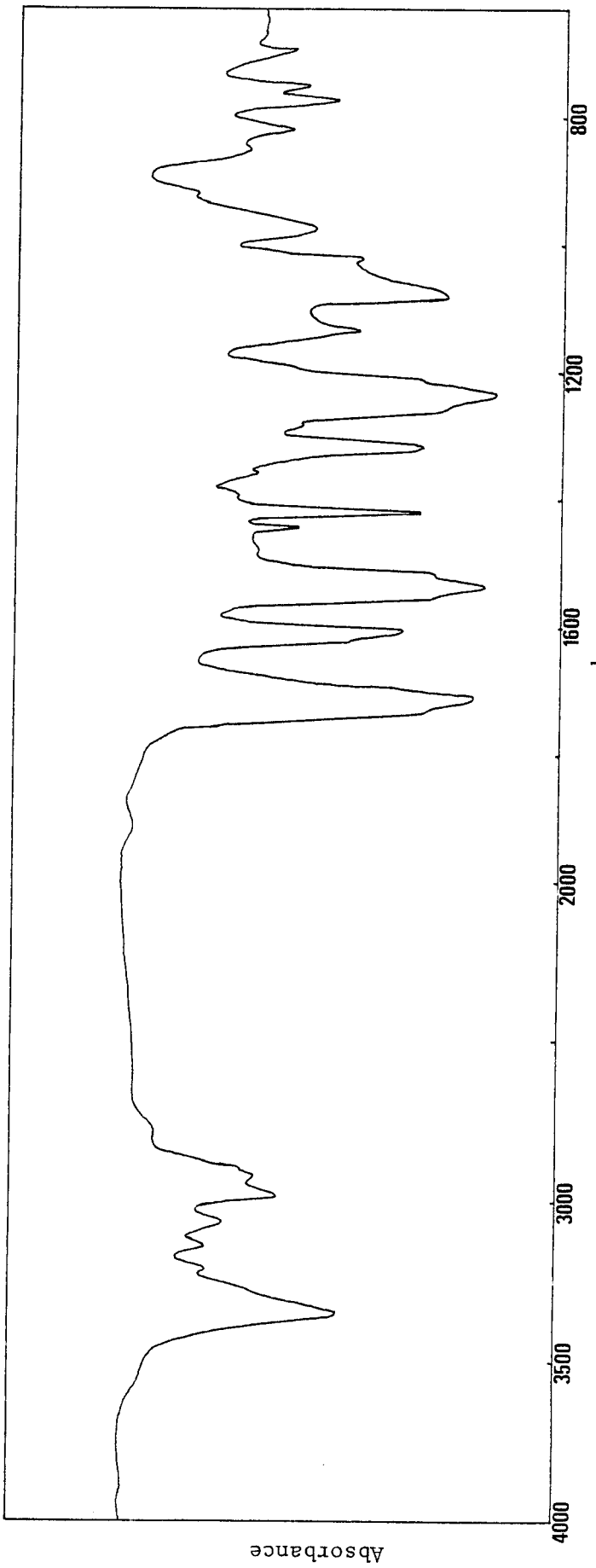


Figure 4.X: Infrared Spectrum of P.U.4(31)

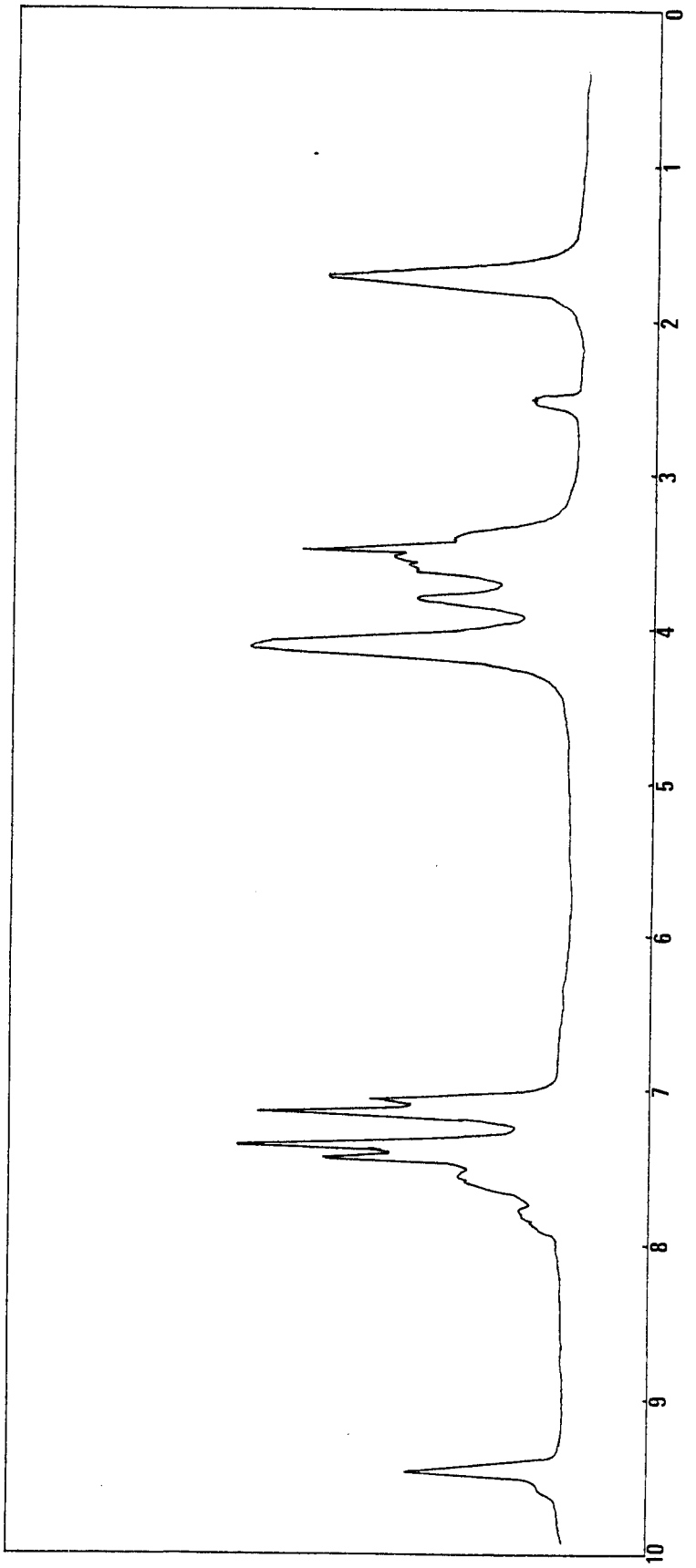


Figure 4.XI: N.M.R. Spectrum of P.U.4(31)

Table 4.ix

Chemical Shift (p.p.m.)	Signal	Assignment
1.70	Broad Singlet	$-OCH_2\underline{CH_2}\underline{CH_2}CH_2O-$ in urethane
3.3-3.7	Broad Multiplet	$-P-O-CH_2\underline{CH_2}O\underline{CH_2}\underline{CH_2}O\underline{CH_2}CH_2-O-P$ in polyester segment
3.80	Broad Singlet	$-OOCNH-C_6H_4-\underline{CH_2}-C_6H_4-NHCOO-$
4.11	Broad Singlet	$-O\underline{CH_2}CH_2CH_2\underline{CH_2}O-$ in urethane
	and	$-P-O-\underline{CH_2}-$ in polyester segment
7.25	AA'BB' Quartet	H_A H_B — CH_2 — H_B H_A / $H_{A'}$ $H_{B'}$ $H_{B'}$ $H_{A'}$
7.7	Broad Multiplet	$-P-C_6H_5$ aromatic protons
9.46	Sharp Singlet	$-\underline{N}H-C(=O)-O-$

Table 4.x

Polyurethane	%C Found (Calculated)	%N Found (Calculated)	%H Found (Calculated)	%P By N.M.R. Found (Calculated)
P.U.4 (31)	62.54 (62.14)	5.98 (5.44)	6.09 (6.02)	2.90 3.06 (3.73)

CHAPTER 5

THERMAL DEGRADATION OF POLY[BUTYLENE PHENYLPHOSPHONATE]

5.1 INTRODUCTION

To simplify the study of the thermal degradation of polyurethanes containing copolymerised phosphorus polyesters, it was important to understand the mechanisms by which these polyester segments degrade. This chapter describes work carried out to determine the thermal degradation properties of poly[butylene phenylphosphonate].

Phosphorus polyester polyols attracted attention in the 1960's after a variety of synthetic routes were reported[35,51]. Unlike organic polyesters and polyethers, this area was not developed successfully and very little attention was paid to the stability or "degradability" of these compounds.

However, two observations were made by Korshak in 1957[52] and 1958[53] during polymerisation experiments. In 1957 distillation of the only product from phenylphosphonic dichloride and 1,4-butanediol produced the cyclic diester, butylene phenylphosphonate in low yields which could not be induced to polymerise. A year later Korshak noticed that polymerising bis(2-chloroethyl) methylphosphonate at 250^{o} caused thermal decomposition to methylphosphonic acid. He did not decide whether polymer or monomer was the source of the acid. Along the same lines Shimidzu et al.[54] reported that hydrolytic degradation of poly[ethylene alkylphosphonate] by sodium hydroxide produced the sodium salt of the corresponding alkylphosphonic acid.

Thermal degradation of poly[butylene phenylphosphonate] was investigated with these few facts in mind.

5.2 THERMAL ANALYSIS OF POLY[BUTYLENE PHENYLPHOSPHONATE]

D.S.C. and D.T.A.

Differential Scanning Calorimetry and Differential Thermal Analysis provided very similar information about the polyol. The D.S.C. trace of poly[butylene phenylphosphonate], illustrated in Figure 5.I, reveals several endothermic reactions during thermal degradation. The major endotherm appears near 240° but other features are obvious before this temperature.

T.G.A.

Thermogravimetry showed clearly three periods of weight loss during thermal degradation. From Figure 5.II, it is obvious that one per cent of the total weight of sample is lost by 150°. From this temperature the weight decreases more rapidly to 200° when ~87% of the polyol remains. Between 200 and 275° the sample is reduced to 65% of its original weight and finally by 550° a residue of ~25% remains.

The T.G. curve and the trace from Thermal Volatilisation Analysis of poly[butylene phenylphosphonate] have been drawn in the same diagram. Although the techniques studied the polyol under a nitrogen atmosphere and a vacuum respectively, useful comparisons were made.

T.V.A.

The T.V.A. trace in Figure 5.II represents the pressures of volatile degradation products as the polyol is heated. The release of volatile products reaches a maximum at 180 and 255° each corresponding to high rates of loss of weight. From 175 to 220° the trace shows a plateau of pressure immediately after the -100° trap. This behaviour is called a limiting rate effect, L.R.E.[20], and is caused by a substance which condenses at -100° but then distils slowly into the -196° trap. The substance responsible for this L.R.E. was identified when polyol was heated to 200° after which analysis of the volatile products indicated tetrahydrofuran only was formed. Further T.H.F. and other volatile products are produced until ~300° at which temperature most of the cold ring fractions begin to appear on the walls of the degradation tube. This loss of material from polyol to the cold ring accounts for the final section of the T.G. curve.

No non-condensable products were recorded during thermal volatilisation.

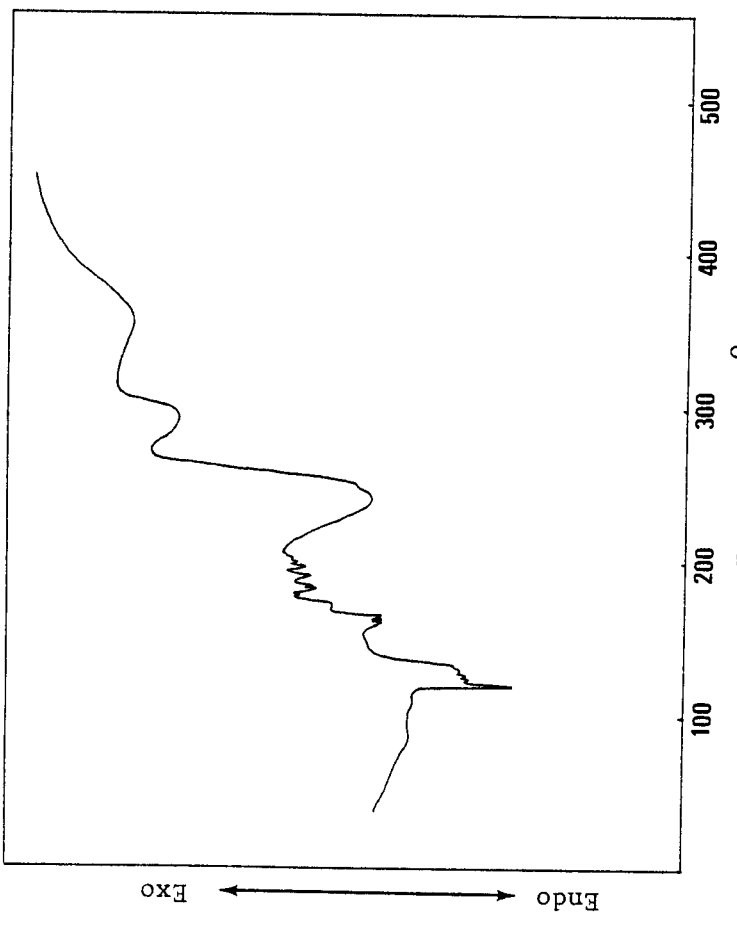
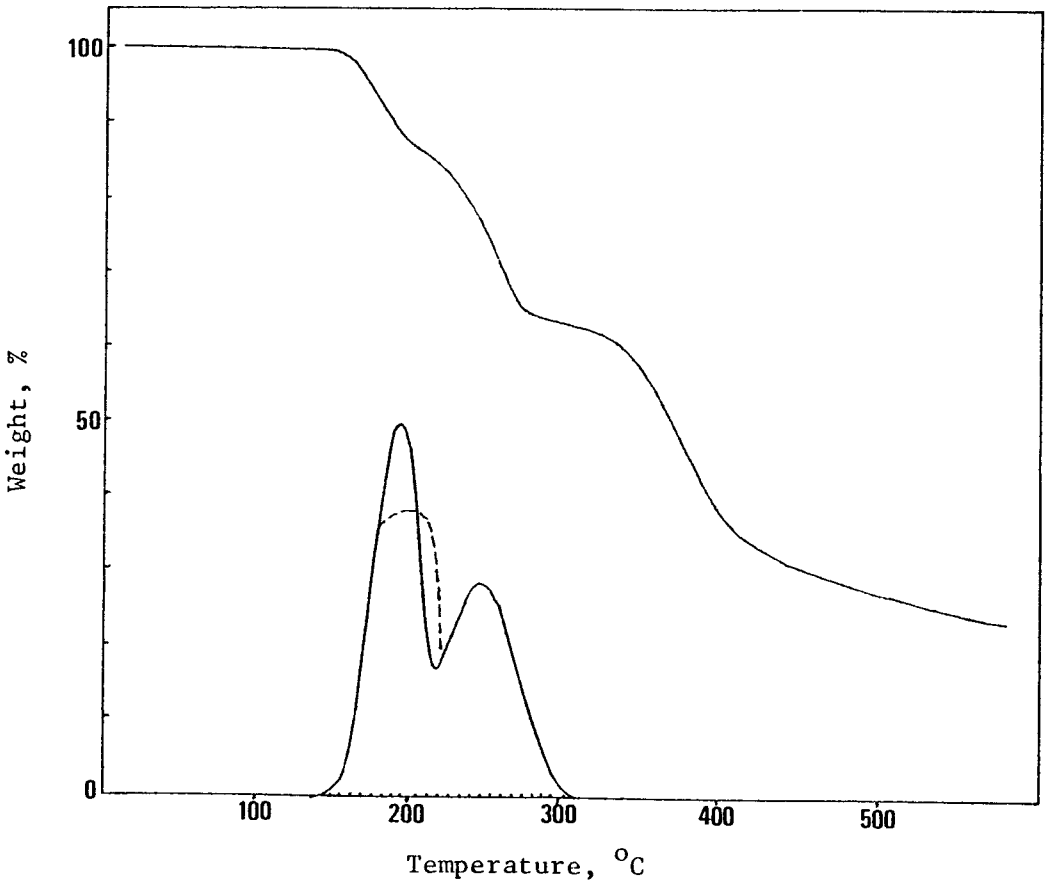


Figure 5.I: D.S.C. Trace of Poly[butylene phenylphosphonate]



T.V.A. Trap Temperatures: ——— = 0, -45 and -75°, ---- = -100°, ····· = -196°

Figure 5.II: T.G. Curve and T.V.A. Trace of Poly[butylene phenylphosphonate]

5.3 ANALYSIS OF PRODUCTS FROM THERMAL DEGRADATION

Products of thermal degradation belong to one of four classes according to their volatility (Chapter 2, page 19).

Condensable Products of Degradation

The subambient distillation technique separated a mixture of five condensables. The trace from subambient distillation of products from 6.5 mg of polyol is drawn in Figure 5.III. Four products identified by infrared were 1,3 butadiene, T.H.F., D.H.F. and water. The final distillation fraction was an unsaturated aliphatic which did not contain phosphorus. However its quantity and low volatility made absolute identification difficult.

Cold Ring Fractions

Three products condensed on the cooler areas of the degradation tube during thermal treatment of polyol.

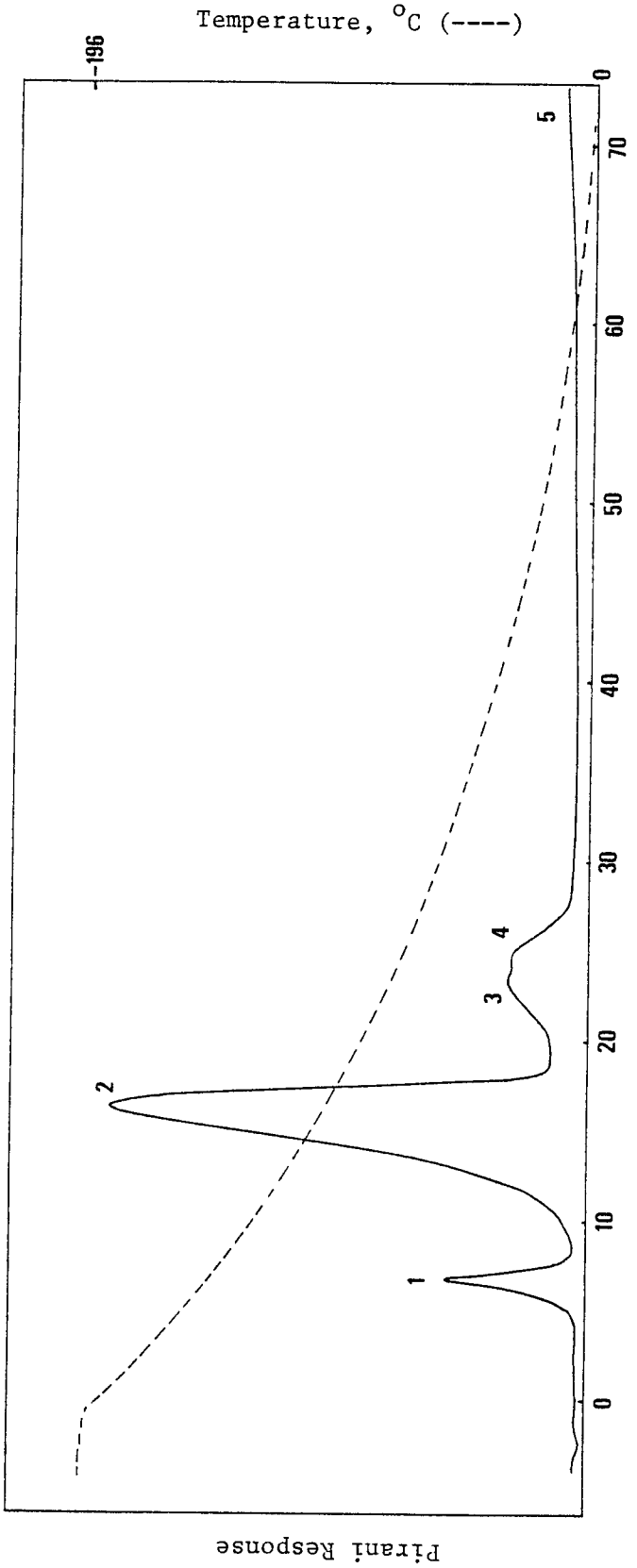
Small deposits of fine white crystals appeared at the top of the tube. This material was easily collected and shown by a combination of I.R., N.M.R. and mass spectrometry to be the cyclic diester of phenylphosphonic acid and 1,4-butanediol. The structure of the diester is drawn in Table 5.i.

The remaining cold ring fraction, a colourless, viscous liquid, was collected by dissolving in chloroform. After several hours a solid crystallised from solution to be identified spectroscopically as phenylphosphonic acid. See Table 5.i.

I.R. and N.M.R. indicated the viscous liquid left in solution was an oligomeric chain with terminal acid groups. The likely diacid ester structure which satisfies N.M.R. integration has been drawn in Table 5.i.

Residue

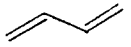
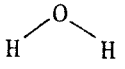
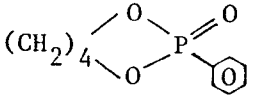
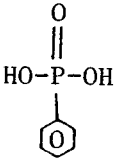
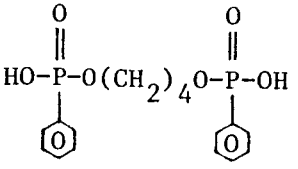
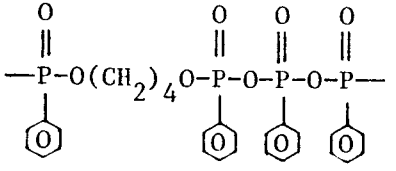
The residue from polyol after thermal degradation was a light brown solid whose absolute structure was not determined. The I.R. spectrum of the residue, drawn in Figure 5.IV, indicates the presence of phosphorus^{V}-phenyl bonds and smaller amounts of butylene links. No hydroxyl or acid groups remain although the absorption at 970 cm^{-1} does suggest that condensed phosphonates, -P-O-P-, are produced[47,55]. Since no evidence of crosslinking was found a linear structure has been suggested in Table 5.i.



Key to Products: 1 = 1,3 Butadiene, 2 = T.H.F., 3 = D.H.F., 4 = Water, 5 = Unidentified

Figure 5.III: Subambient Trace of Poly[butylene phenylphosphonate]

Table 5.i: Products from Thermal Degradation of Poly[butylene phenylphosphonate]

	Degradation Product from Poly[butylene phenylphosphonate]	Structure	Remarks
Condensables	1,3-butadiene		
	Tetrahydrofuran		
	Dihydrofuran		
	Water		
	Unsaturated Aliphatic	———	
Cold Ring Fractions	Butylene phenylphosphonate diester		m.pt. 71.5-2° literature[52] 76-7.5°
	Phenylphosphonic Acid		m.pt. 160-3° literature[97] 158° 46.8% of theoretical yield
	Oligomeric Diacid		
Residue	Crystalline Solid		

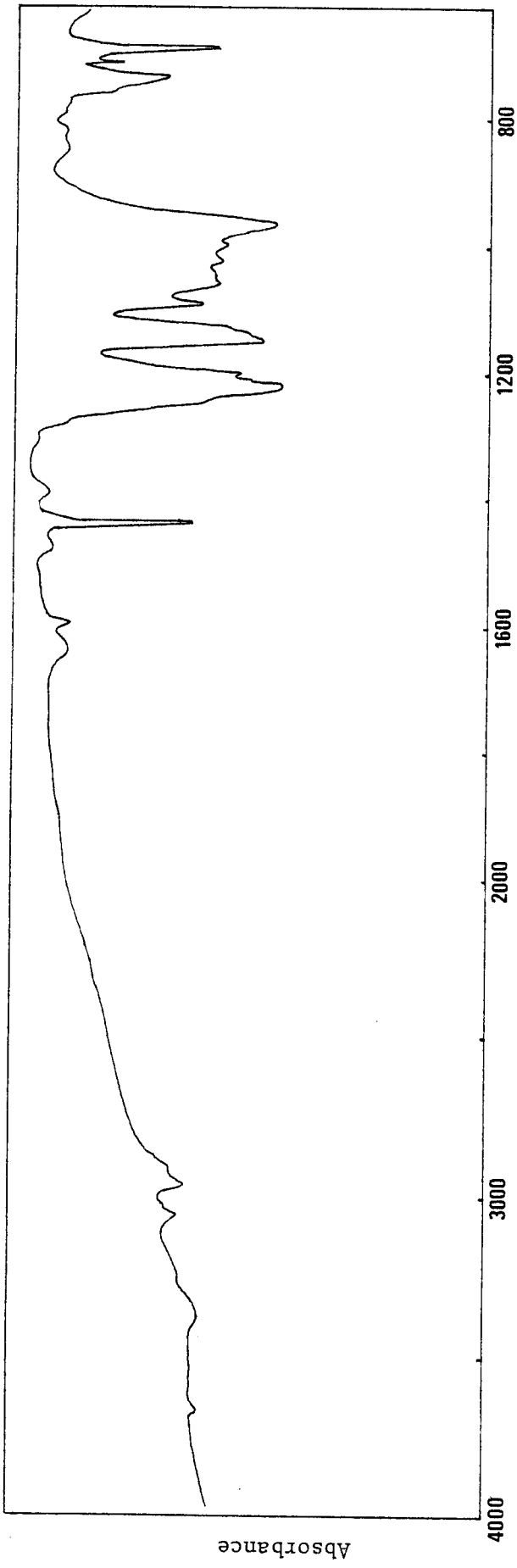


Figure 5.IV: Infrared Spectrum of Residue from Poly[butylene phenylphosphonate]

5.4 THERMAL DEGRADATION OF POLY[BUTYLENE PHENYLPHOSPHONATE]BIS [PHENYLCARBAMATE]

To obtain more information on the role of the terminal hydroxyl group during thermal degradation some polyol was reacted at 70° in D.M.F. solution with two molar equivalents of phenyl isocyanate until N.M.R. and I.R. confirmed each end group had been converted to its phenylcarbamate derivative. The solid product, poly[butylene phenylphosphonate]bis[phenylcarbamate] (P.B.C.), was then studied by T.G., D.S.C. and T.V. and results compared with those from the original polyol.

D.S.C.

The D.S.C. trace in Figure 5.V shows that the biscarbamate undergoes major endothermic degradation between 200 and 260°. Blocking the hydroxyl end groups on the polyol appears to eliminate most of the endotherm at 116° and erratic behaviour between 150 and 200° found in Figure 5.I.

T.G.A.

The T.G. curve drawn in Figure 5.VI shows that loss of weight from P.B.C. proceeds in two stages which start at ~175 and ~300°. Only 11% of the original weight remains at 525°. The derivatives of the T.G. curves of biscarbamate and polyol are also illustrated. They help to highlight the similarities and major difference between the thermal behaviour of polyol and P.B.C.

T.V.A.

When the polyol which has been endcapped is heated under vacuum, volatile materials begin to appear around 190°. At 250° their rate of production has reached a maximum and by 320° this has returned to zero. This behaviour is represented by the T.V.A. trace in Figure 5.VII. Initial production of T.H.F. between 160 and 220° which is a feature of the uncapped polyol is not apparent.

Analysis of condensables collected after thermal degradation of P.B.C. revealed CO_2 and aniline in addition to 1,3 butadiene, T.H.F., water and a substantial quantity of D.H.F. This information allows a full interpretation of the T.V.A. trace.

The thermal volatilisation system which operated with four parallel limbs and trap temperatures of 0, -45, -75, -100 and -196°, has been described in Chapter 2, page 18. The baseline trace confirms

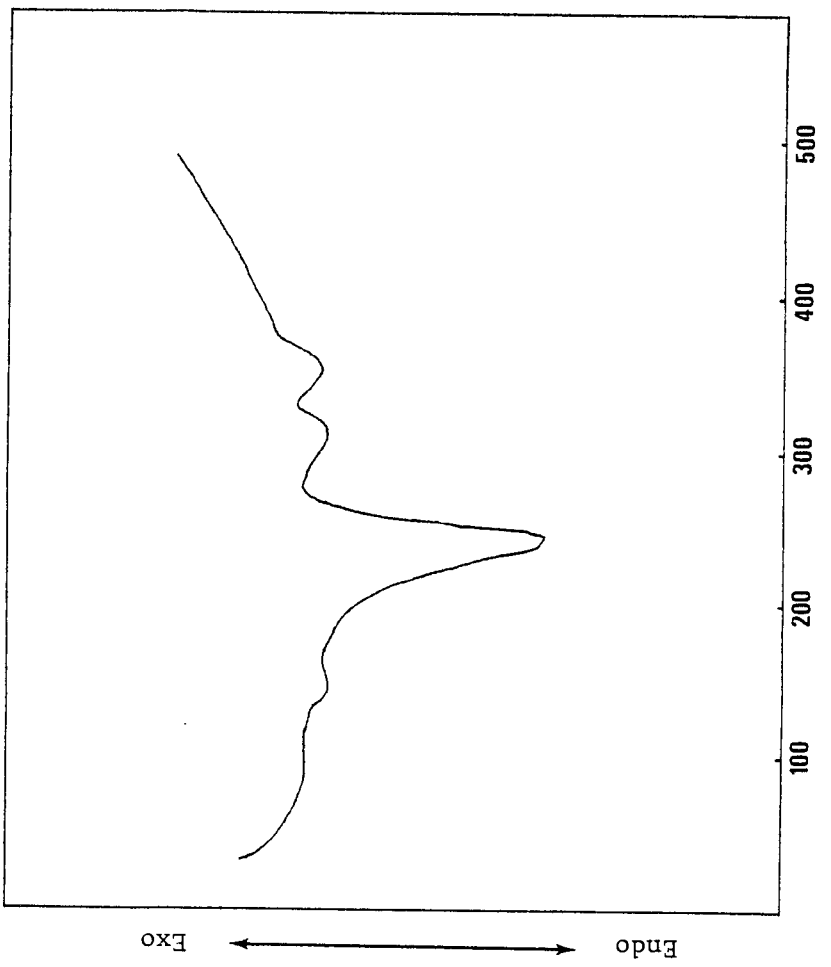
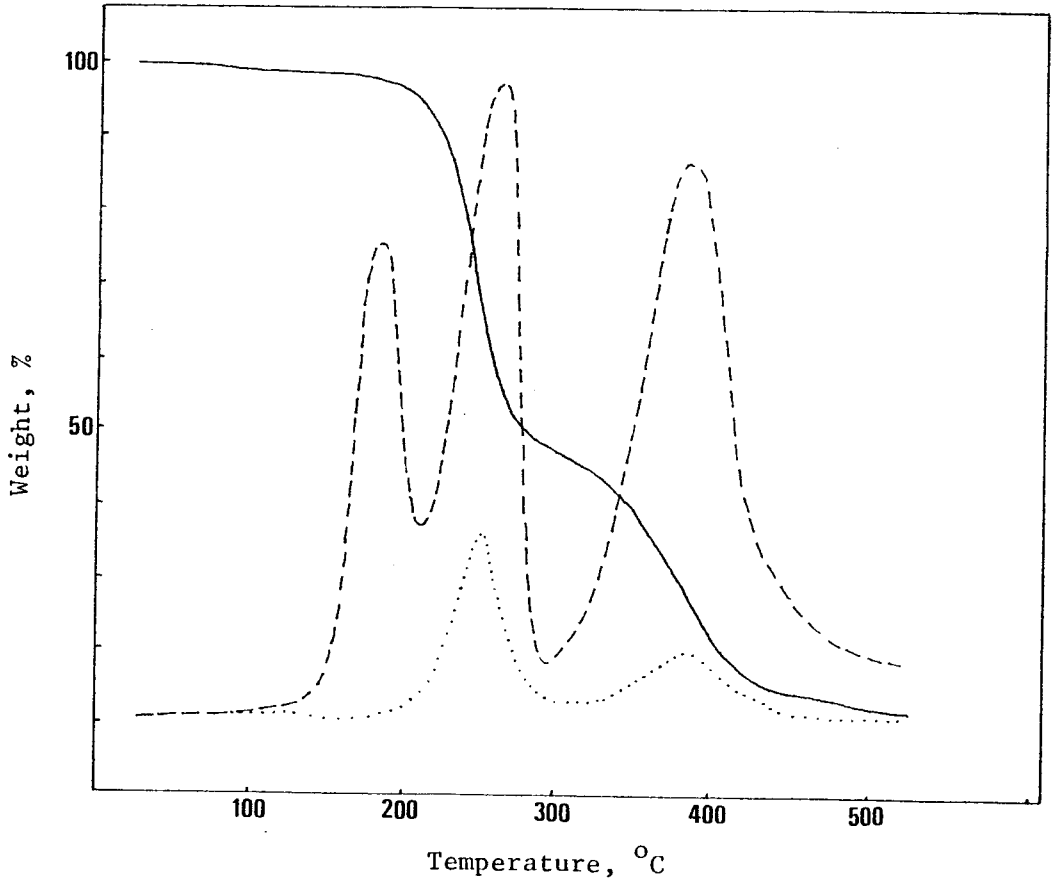
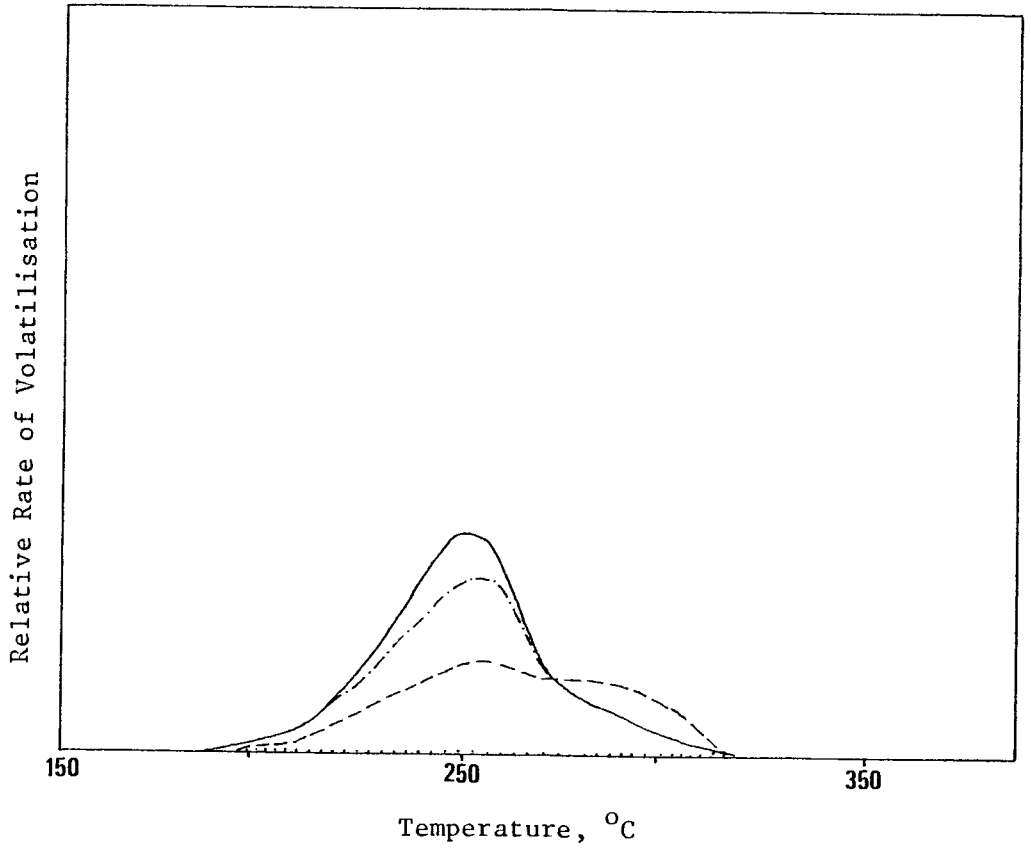


Figure 5.V: D.S.C. Trace of P.B.C.



—— = T.G. Curve, ····· = Derivative Curve, ---- = Derivative of T.G. Curve of Polyol

Figure 5.VI: T.G. Curve of P.B.C.



Trap Temperatures: —— = 0 and -45°, -·-·- = -75°, ---- = -100°, ····· = -196°

Figure 5.VII: T.V.A. Trace of P.B.C.

no non-condensable gas is produced by thermal degradation. 1,3 butadiene and carbon dioxide pass through the 0, -45, -75 and -100° traps and are recorded equally by each of the corresponding traces. However the major volatile product, T.H.F., is condensed initially at -100°. The pressure immediately after the -100° trap is therefore lower than that after the warmer traps; however a L.R.E. is established later when T.H.F. distils from the -100° trap at a steady pressure.

The trace describing pressure immediately after the -75° trap does not maintain its coincidence with those from the 0 and -45° traps because of the presence of D.H.F. which is condensed at -75°. Water and aniline are not produced in sufficient quantity during T.V.A. to affect the trace. The complete T.V.A. trace implies that CO_2, 1,3 butadiene, T.H.F. and D.H.F. appear simultaneously from 200° but D.H.F. is no longer produced in significant amounts after 270°.

5.5 DISCUSSION

More effort has been spent on the synthesis and thermal degradation of simple phosphonic acid derivatives than on polyphosphonate esters. The following information helped to rationalise the results of thermal degradation of poly[butylene phenylphosphonate] and suggest a mechanism which may operate.

Thermal decomposition of alkylphosphonic acid diesters was described by Canavan[55] in 1962 as a new route to alkylphosphonic acids. Heating di-n-butyl ethylphosphonate under nitrogen produced ethylphosphonic acid in 99% yield and but-1-ene by a cis 1,2-elimination.

The acid functions of phosphonic acid esters are known to condense on heating to pyrophosphonic acid diesters and water although room temperature is sufficient with a dehydrating agent[56,57]. Phenyl phosphonic acid condenses in similar fashion after 200°[58] to give pyrophosphonic acid while higher order polyphosphonic acid results from prolonged high temperatures[59]. Finally T.H.F. is a familiar product of catalytic and thermal decomposition of esters and polyesters synthesised from 1,4-butanediol[60,61].

Most of the products of thermal degradation reported in this chapter have been anticipated in literature. A mechanism of thermal degradation of poly[butylene phenylphosphonate] which accounts for these products has been summarised in Figure 5.VIII. The rearrangement prior to ring closure to D.H.F. could be 1,3 sigmatropic shift but this is unlikely when acid is present[62].

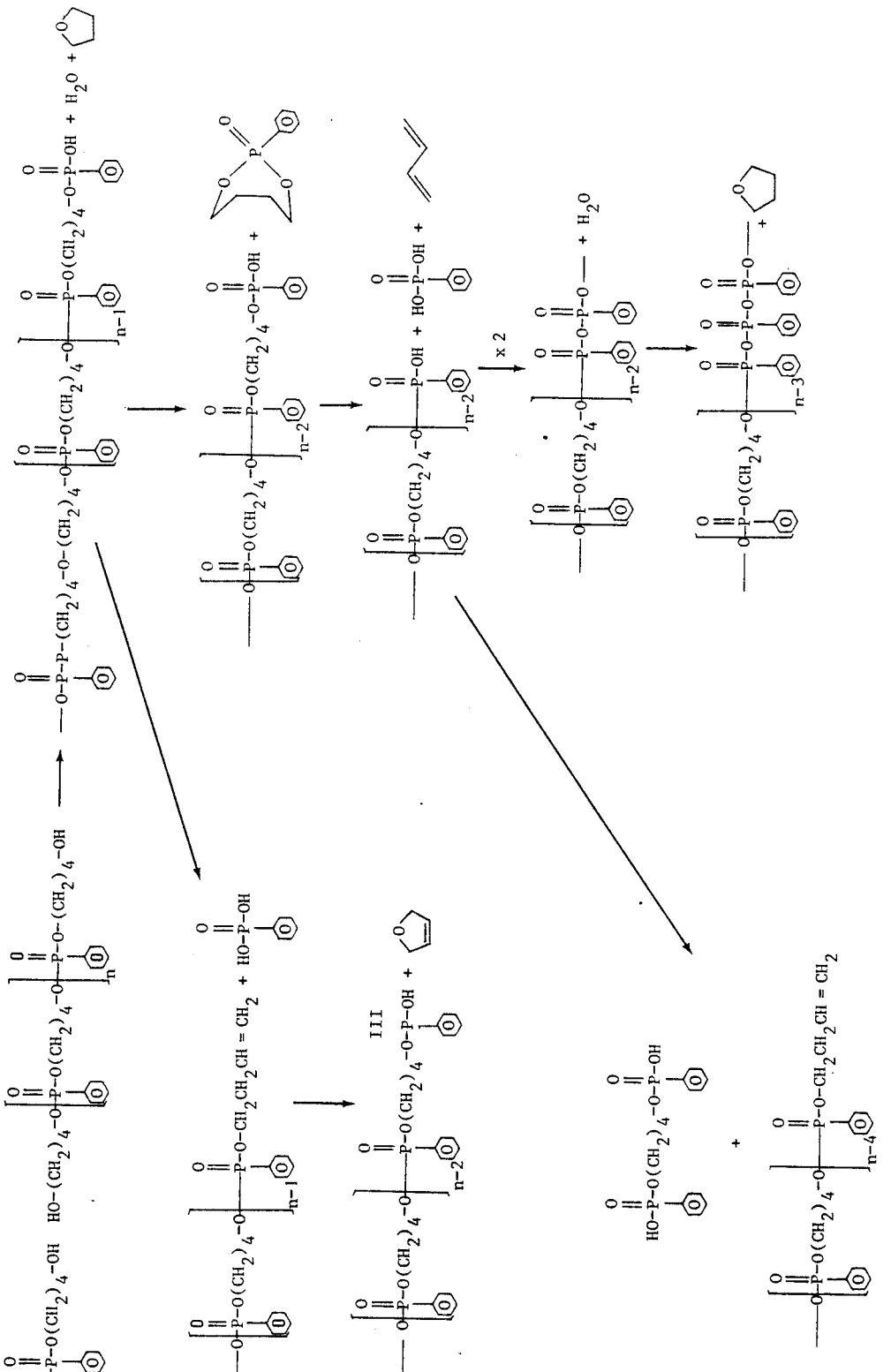


Figure 5.VIII: Proposed Mechanism of Thermal Degradation of Poly[butylene phenylphosphonate]

The facility of each reaction mechanism, listed in Table 5.ii, and the study of P.B.C. and polyol has provided a picture of the degradation of poly[butylene phenylphosphonate] when heated at a rate of 10^{o} per minute under inert atmosphere or vacuum. As polyol is heated initial reaction involves the hydroxyl end groups. Intermolecular condensation occurs to a small extent causing the number average molecular weight of the polyester to rise[63] , however the dominant change between 160^{o} and 200^{o} is loss of tetrahydrofuran from the end of each molecule to leave terminal phosphonic acid functions. (The terminal 4-hydroxybutylene groups account for ~14% of polyol weight; T.G. indicates ~13% of weight is lost by 200^{o}.)

Since phosphoric acids are reported to hydrolyse such systems[35] the new functionality infers that subsequent degradation is autocatalytic. The cyclic diester, observed soon after 200^{o} is probably generated at the chain ends where the molecule is free to adopt the appropriate conformation. The production of T.H.F. increases rapidly again from 200 to 240^{o} leaving pyrophosphonic acid links in the modified back-bone while syn 1,2-elimination at adjacent phosphorus atoms creates small amounts of 1,3 butadiene. The route to D.H.F. from the polyol begins with syn 1,2-elimination at one site followed by acid induced rearrangement before 1,3 butadiene can form. As degradation proceeds the preponderance of acid groups increases the likelihood of condensation and water may still be produced at 300^{o}. Volatile products of degradation do not appear after 300^{o} but the modified polyol continues to lose weight as short oligomers, probably the diacid ester of B.D., and free phenylphosphonic acid volatilises out of the hot zone. By 550^{o} the residue contains regions of condensed phenylphosphonic acid and small sections of polyester still intact.

Thus to summarise, the reaction of polyol to heat involves loss of aliphatic components in several forms to leave involatile condensed phosphonic acids and high boiling free phenylphosphonic acid and its esters. The reactive nature of acid suggests that these products may be significant if generated during the early stages of the thermal degradation of polyurethane 1.

Table 5.ii: List of Reaction Mechanisms During Thermal Degradation of Poly[butylene phenylphosphonate]

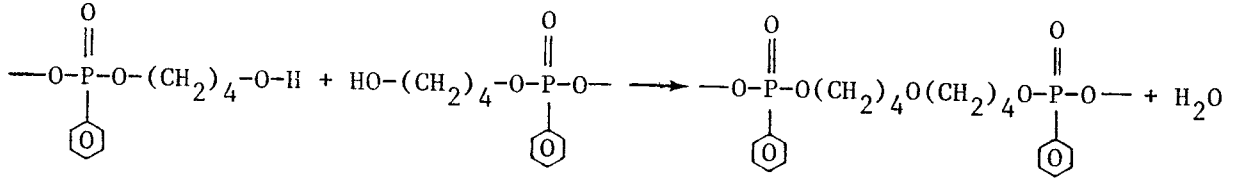
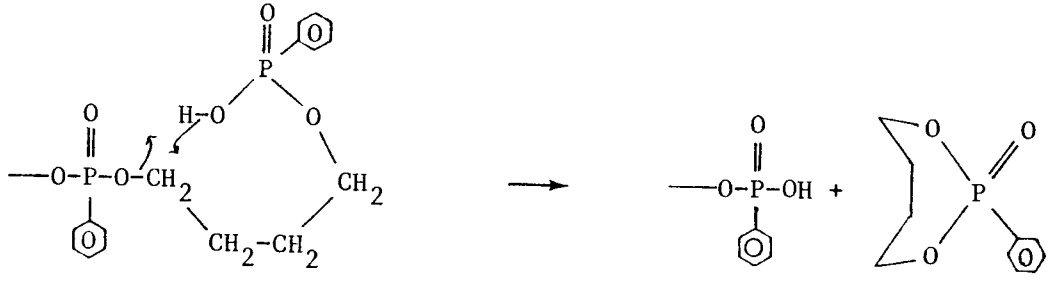
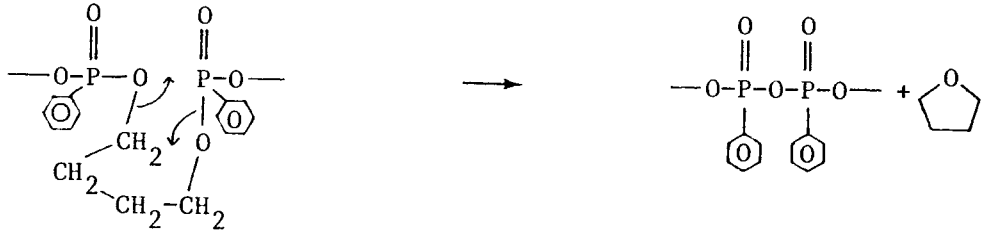
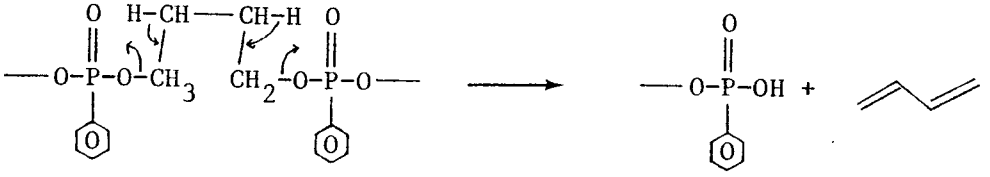
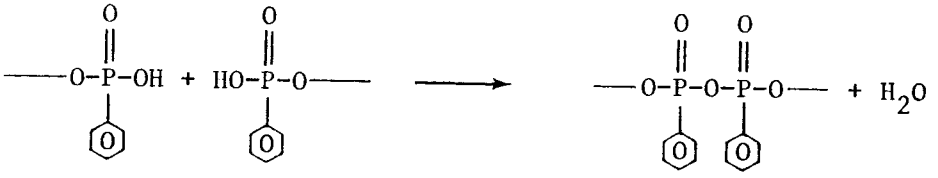
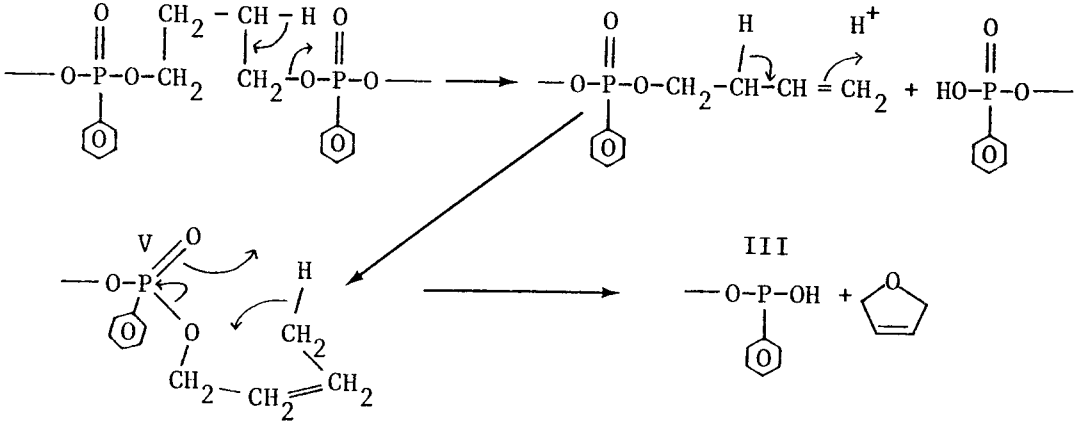
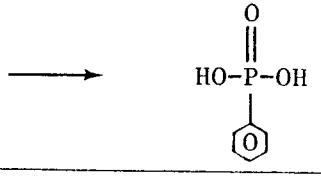
Mechanism Number		Reference
1		38
2		16
3		53
4		60 61

Table 5.ii (continued)

Mechanism Number		Reference
5		55
6		58 59
7		
8	Various combinations of 2,3,5,7 	

CHAPTER 6

THERMAL DEGRADATION OF POLYURETHANE 1

6.1 INTRODUCTION

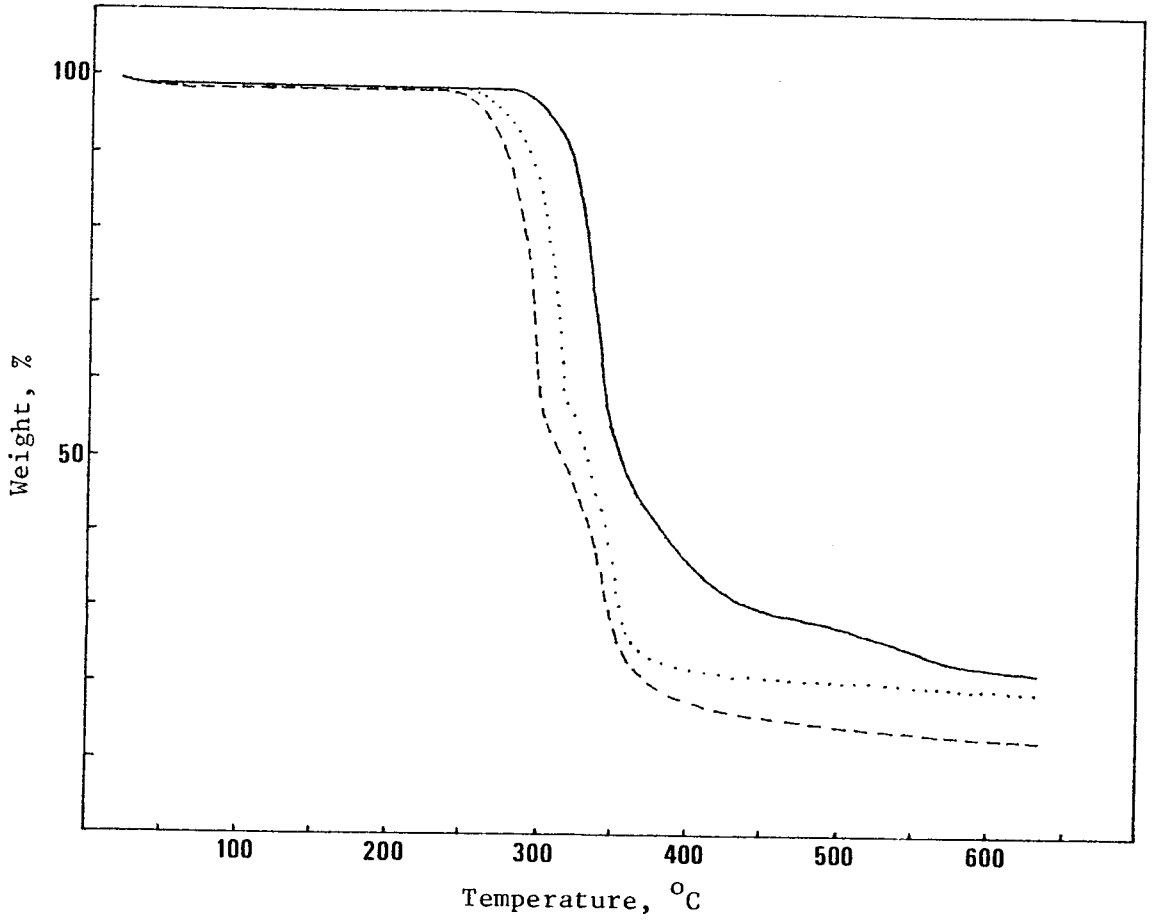
As mentioned in Chapter 5 many varieties of polyesters containing phosphorus have been synthesised but reports of polyesterurethanes therefrom are not as common. Those which have been found describe polymerisation of equimolar amounts of two monomers giving the polyurethane a regular repeat unit[40,64,65]. Any subsequent thermal analysis has always been very modest.

It was felt that a more thorough characterisation of the thermal degradation of polyurethane containing copolymerised phosphorus was required and if possible to express it as a function of phosphorus concentration. This chapter relates the thermal degradation of six polyurethanes, $P.U.1_{(0)}$ - $P.U.1_{(111)}$ described in Chapter 4, page 56, which have similar chemical structures but contain different amounts of copolymerised phosphorus. The polyurethanes have been studied closely and their corresponding properties compared under the appropriate subtitle.

6.2 THERMAL ANALYSIS OF POLYURETHANE 1

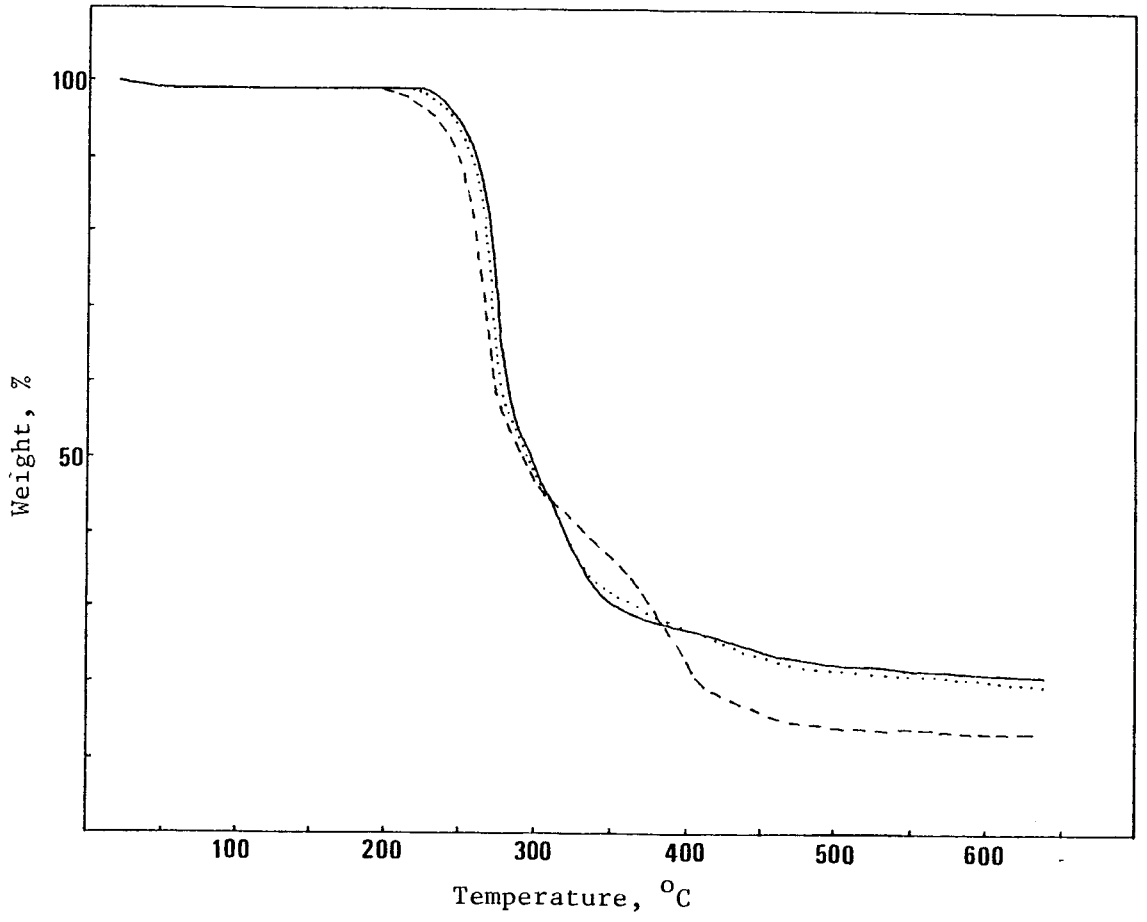
T.G.A.

When heated under a nitrogen atmosphere, Polyurethane 1 begins to lose weight somewhere between 185 and 275°. The thermogravimetric curve suggests that degradation proceeds in two stages emphasized by two maxima in the derivative curve. Figure 6.I shows the T.G. curves of Polyurethanes 1 degraded under dynamic nitrogen and indicates that the temperature of initial loss of weight from Polyurethane 1 bears an inverse relationship to the amount of copolymerised phosphorus



T.G. curves: ——— = $P.U.I_{(0)}$, ... = $P.U.I_{(11)}$, ------ = $P.U.I_{(22)}$

Figure 6.I(a): Thermogravimetric Curves of Polyurethane I



T.G. curves: ——— = $P.U.I_{(44)}$, ····· = $P.U.I_{(54)}$, ------ = $P.U.I_{(111)}$

Figure 6.I(b): Thermogravimetric Curves of Polyurethane I

polyester. A similar relationship between weight of residue and polyester content was not so apparent.

T.G.A. curves of Polyurethane 1 under reduced pressure (1 torr) have profiles similar in five cases to those recorded under nitrogen. $P.U.1_{(0)}$ lost weight in a single step[16]. However under vacuum the polymer starts to lose weight at lower temperatures than under nitrogen and leaves a residue of consistently smaller percentage weight.

The features of thermogravimetric analysis of Polyurethane 1 under both conditions are summarised in Table 6.i and percentage weights of residues plotted as functions of phosphorus content in Figure 6.II. Charring experiments described by Papa[15] which involved heating samples isothermally at 300° for 45 minutes in air were carried out to supplement the results. The weight of residue in air (char) is expressed as a percentage of original weight in Table 6.i and included in Figure 6.II.

D.S.C. and D.T.A.

Similar information about Polyurethane 1 was provided by the two techniques, D.T.A. and D.S.C., and since the latter was more sensitive only those results are reported here.

Four D.S.C. traces of Polyurethane 1 are drawn in Figure 6.III. The endotherm at 220° in Figure 6.III(a) corresponds to the melting temperature but while the same feature is exhibited by $P.U.1_{(11)}$ and $P.U.1_{(22)}$ the remaining polyurethanes do not possess a melting temperature below that of their degradation. The simple endothermic degradation expected from $P.U.1_{(0)}$[16] is confirmed but a more complicated profile is found when the remaining members of the polyurethane series are scanned. When Polyurethane 1 containing small amounts of phosphorus polyester segments is heated, the main endothermic degradation is interrupted briefly by a sharp exothermic spike (Figure 6.III(b)) and if phosphorus is present in the polyurethane in larger concentrations degradation proceeds via two distinct endothermic processes.

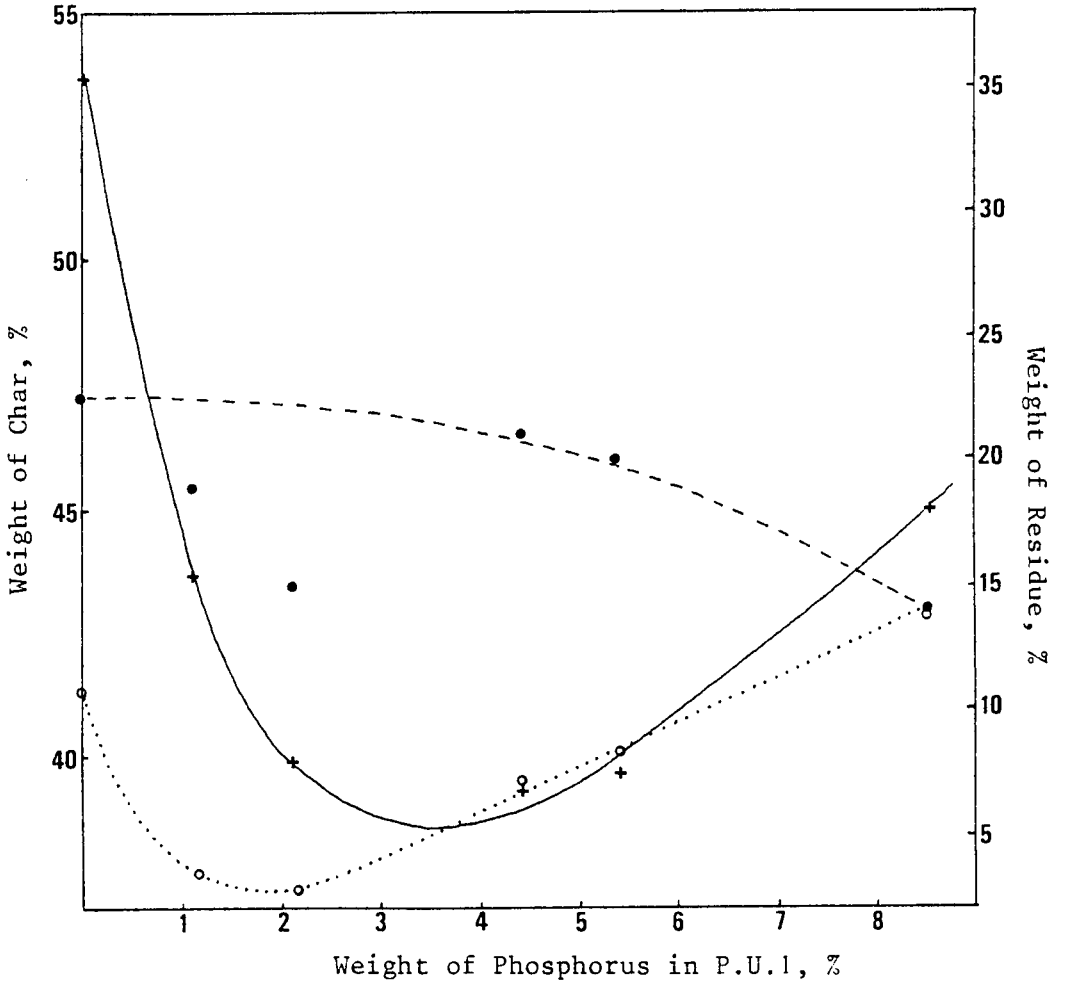
Inspection shows that the single or double endotherm from each sample of polyurethane always corresponds closely to the first stage of weight loss thereby ratifying the inverse relationship between phosphorus content of the polymer and its thermal stability mentioned in Section 6.1.

T.V.A.

When it is heated under vacuum, Polyurethane 1 starts to release

Table 6.i: Thermal Parameters from Thermogravimetric Analysis of Polyurethane 1

P.U.	UNDER NITROGEN				UNDER VACUUM		
	Temperature of Initial Weight Loss °C	Temperature of First Maximum Rate of Weight Loss °C	Temperature of Second Maximum Rate of Weight Loss °C	Residue at 600° %	Temperature of Initial Weight Loss °C	Residue %	Weight of Char %
0	263	338	375	22.5	238	10.6	53.6
11	245	313	352	19	212	3.4	43.6
22	235	299	343	15	207	2.8	39.9
44	200	272	312	21	183	7.1	39.3
54	200	270	308	20	178	8.5	39.6
111	185	265	388	14	153	13.7	45.0

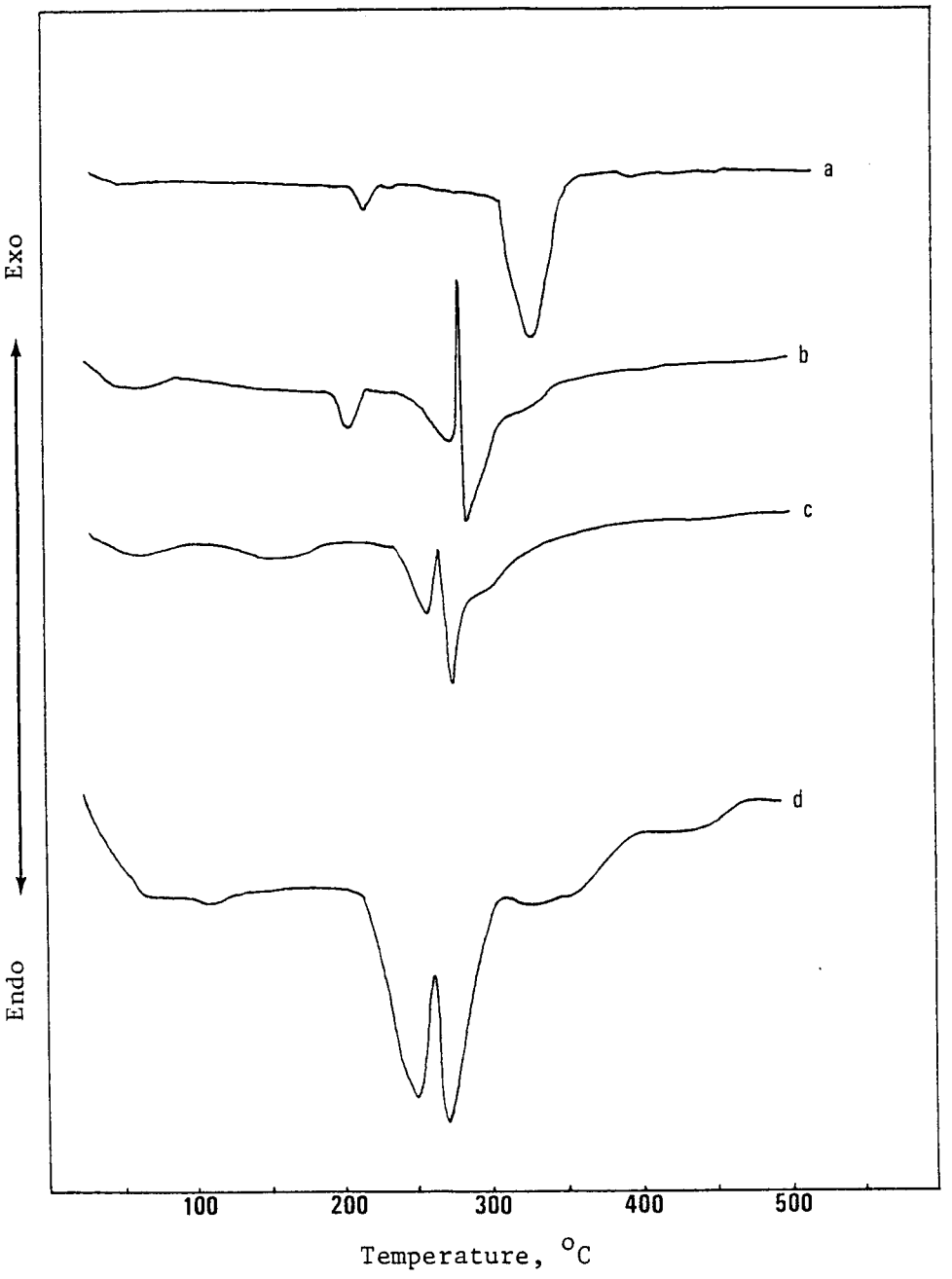


Key to curves: ------ = Weight of Residue under Nitrogen

..... = Weight of Residue under Vacuum

——— = Weight of Char

Figure 6.II: Residue and Char as Functions of Phosphorus Content



D.S.C. traces: a = P.U.1$_{(0)}$, b = P.U.1$_{(22)}$

c = P.U.1$_{(54)}$, d = P.U.1$_{(111)}$

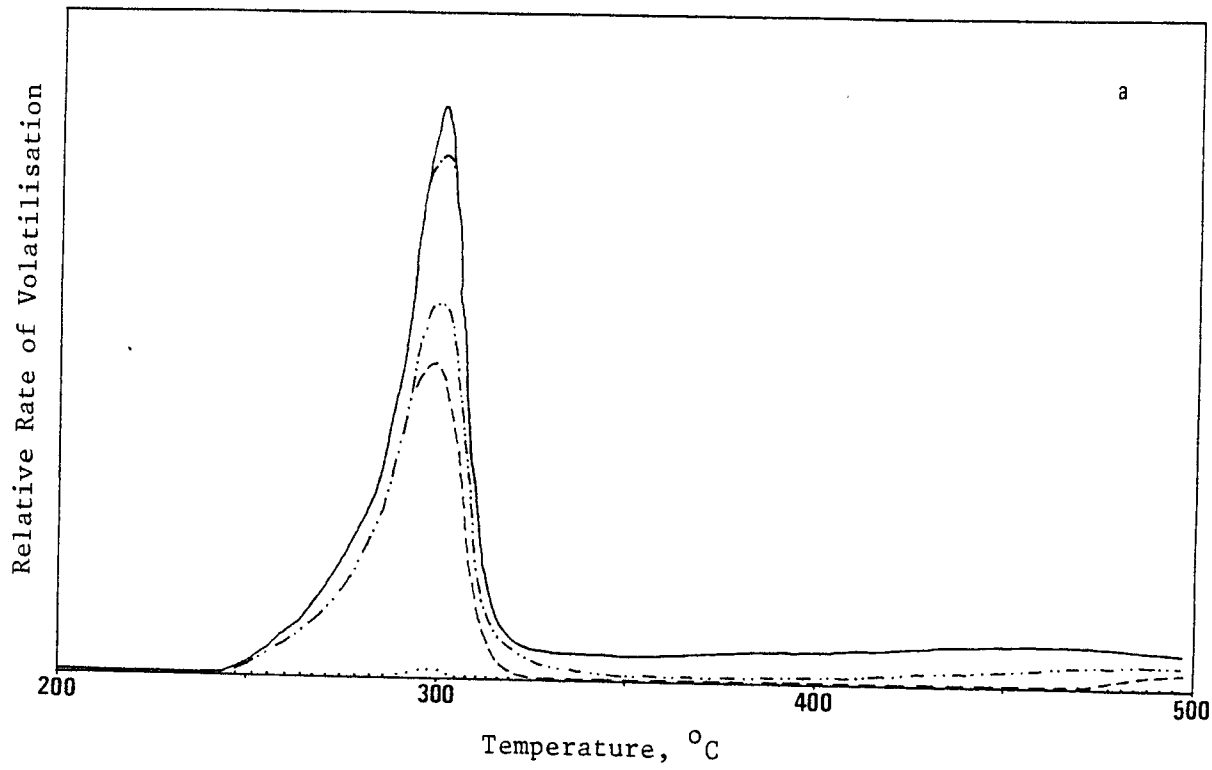
Figure 6.III: D.S.C. Traces of Polyurethane 1

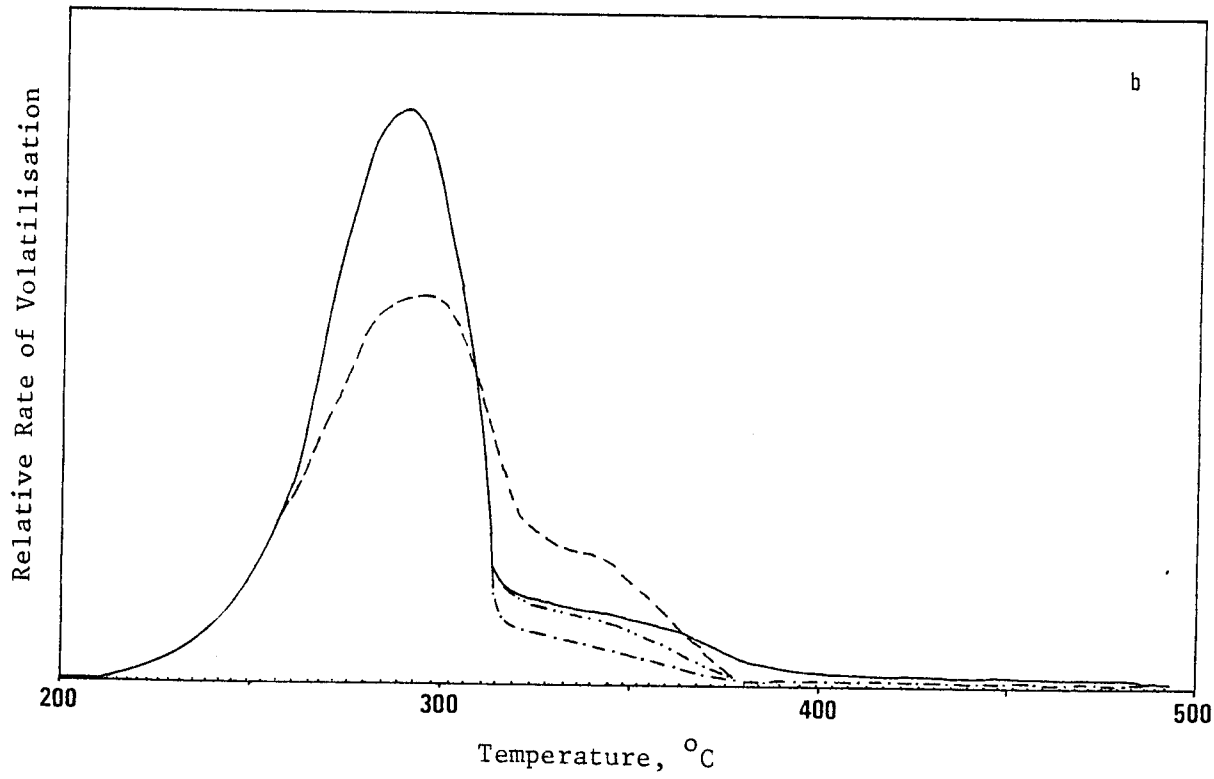
volatile products in the range 170-240°. The exact temperature at which this degradation commences can be seen for four examples in Figure 6.IV.

The thermogram of P.U.1$_{(0)}$ has been published[16] and indicates a release of volatile products of degradation from 240°. The separation of the respective temperature traces indicates that a variety of condensables of different volatilities must be produced. The simple appearance of the thermogram in Figure 6.IV(b) is a result of extensive production of carbon dioxide and tetrahydrofuran by P.U.1$_{(11)}$. Their presence obscures any evidence of other products until the polymer reaches ~325° when some material is condensed at -45°. The limiting rate effect at -100° and even at -75° reflects the behaviour of T.H.F. (see Chapter 5, page 80). Figure 6.IV(c) resembles closely Figure 6.IV(b) and suggests that a similar degradation process operates despite a fourfold increase in the amount of copolymerised polyphosphonate from P.U.1$_{(11)}$ to P.U.1$_{(44)}$. Volatile materials from P.U.1$_{(44)}$ are detected over a narrow range (185-320°) which is also a characteristic of P.U.1$_{(22)}$ and P.U.1$_{(54)}$. These three polymers respond to heat by a brief but furious expulsion of gases.

The thermogram in Figure 6.IV(d) is most complicated showing two separate periods when the rate of evolution of volatile products of degradation reaches a maximum. The first stage of degradation of P.U.1$_{(111)}$, indicated by the appearance of condensables, begins about 170° which conforms to the apparent trend in Table 6.ii. However from 245° when the rate of liberation of volatile products from the polymer is a maximum, significant quantities of high boiling materials are also generated. These are responsible for the separation on the thermogram of the traces corresponding to 0, -45 and -75° traps. A L.R.E. at the -100° trap is just discernable before the -100 and -75° traces return to coincidence near the baseline. The second stage of degradation indicated by the T.V.A. trace of P.U.1$_{(111)}$ operates around 430° where the rate of evolution of volatile products is a maximum. At these elevated temperatures the sample will have changed considerably from the original polyurethane.

For Polyurethane 1 the temperatures which correspond to features on the T.V.A. traces are compiled in Table 6.ii. The effect of phosphorus on the thermal stability of poly[butylene methylene bis(4-phenylcarbamate)] (P.U.1$_{(0)}$) is obvious.

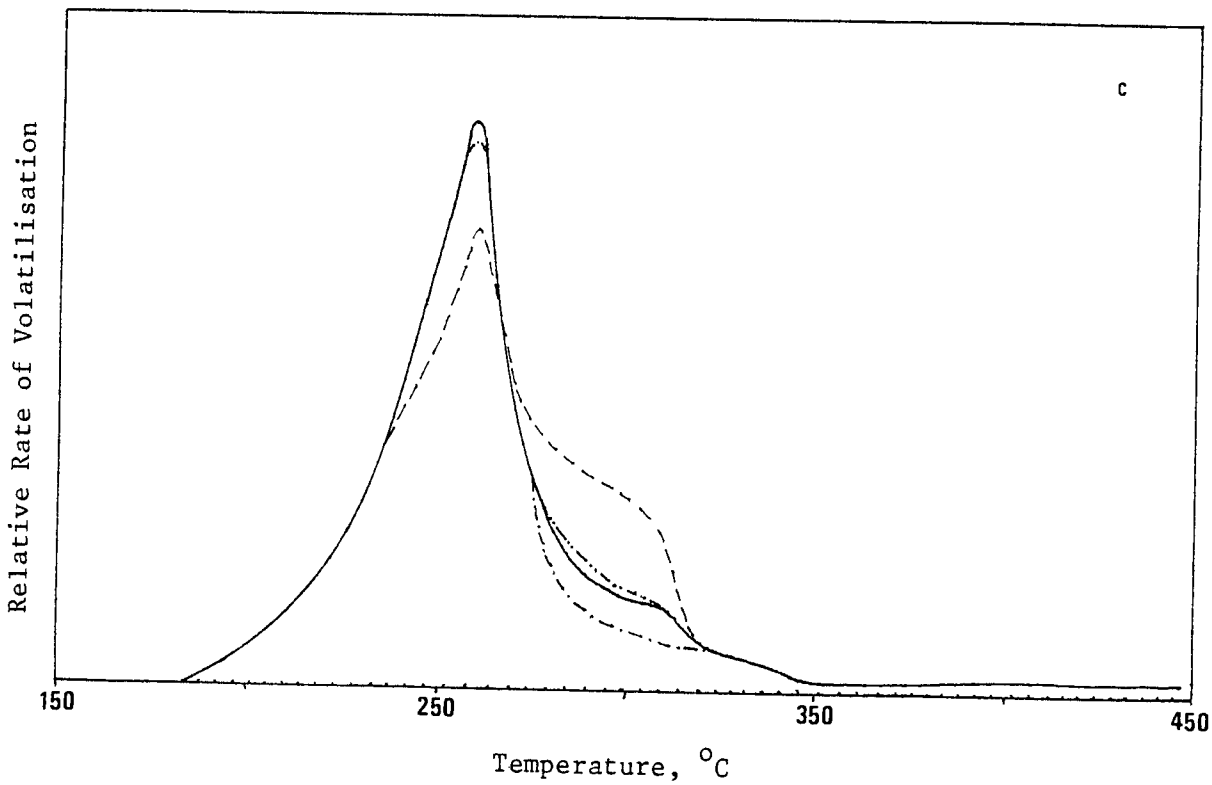




Trap Temperatures, °C: —— = 0, -·-·- = -45, ····· = -75,
– – – – = -100, ····· = -196

T.V.A. Curves: a = P.U.1$_{(0)}$, b = P.U.1$_{(11)}$

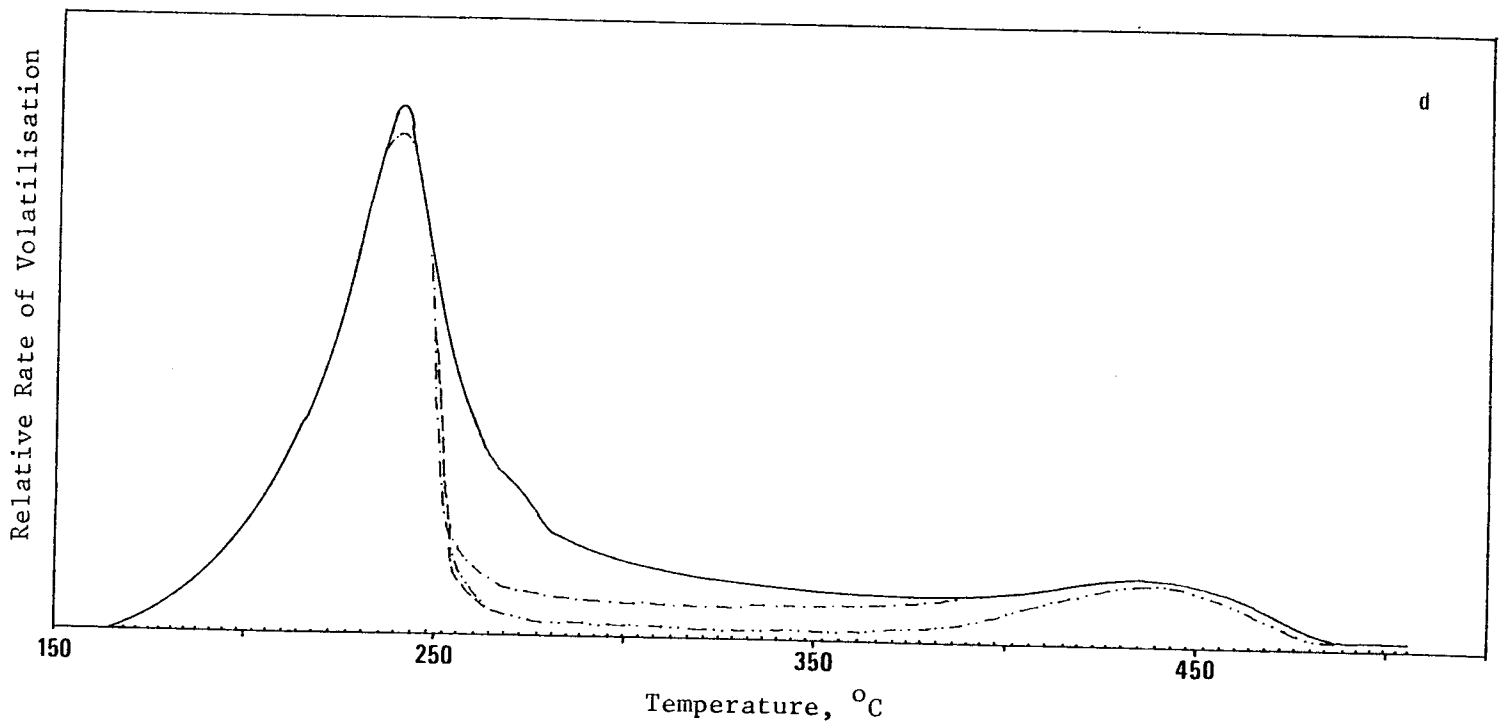
Figure 6IV(a),(b): T.V.A. Curves of Polyurethane 1



Trap Temperatures, °C: —— = 0, -·-·- = -45, -···- = -75,
----- = -100, ····· = -196

T.V.A. Curves: c = P.U.I$_{(44)}$

Figure 6.IV(c): T.V.A. Curves of Polyurethane I



Trap Temperatures, °C: ——— = 0, -·-·- = -45, -·-·-·- = -75, ---- = -100, ····· = -196

T.V.A. Curves: d = $P.U.1_{(111)}$

Figure 6.IV(d): T.V.A. Curves of Polyurethane 1

Table 6.ii: Thermal Parameters from Thermal Volatilisation Analysis of Polyurethane 1

Polyurethane	Initial evolution of volatile products (temperature, ^{o}C)	Maximum rate of evolution of volatile products (temperature, ^{o}C)	Second maximum rate of evolution of volatile products (temperature, ^{o}C)
$P.U.1_{(0)}$	240	300	-
$P.U.1_{(11)}$	205	290	-
$P.U.1_{(22)}$	190	283	-
$P.U.1_{(44)}$	185	260	-
$P.U.1_{(54)}$	172	255	-
$P.U.1_{(111)}$	162	240	440

6.3 ANALYSIS OF PRODUCTS FROM THERMAL DEGRADATION

The products from thermal degradation of Polyurethane 1 have been identified and are reported under the appropriate title according to their volatilities (see Chapter 2, page 19).

Non-Condensable Products of Degradation

The T.V.A. thermograms in Figure 6.IV show that only $P.U.1_{(0)}$ degrades to give non-condensable gas, identified as carbon monoxide. When the polyurethane contains phosphorus no permanent gas is detected during or after degradation.

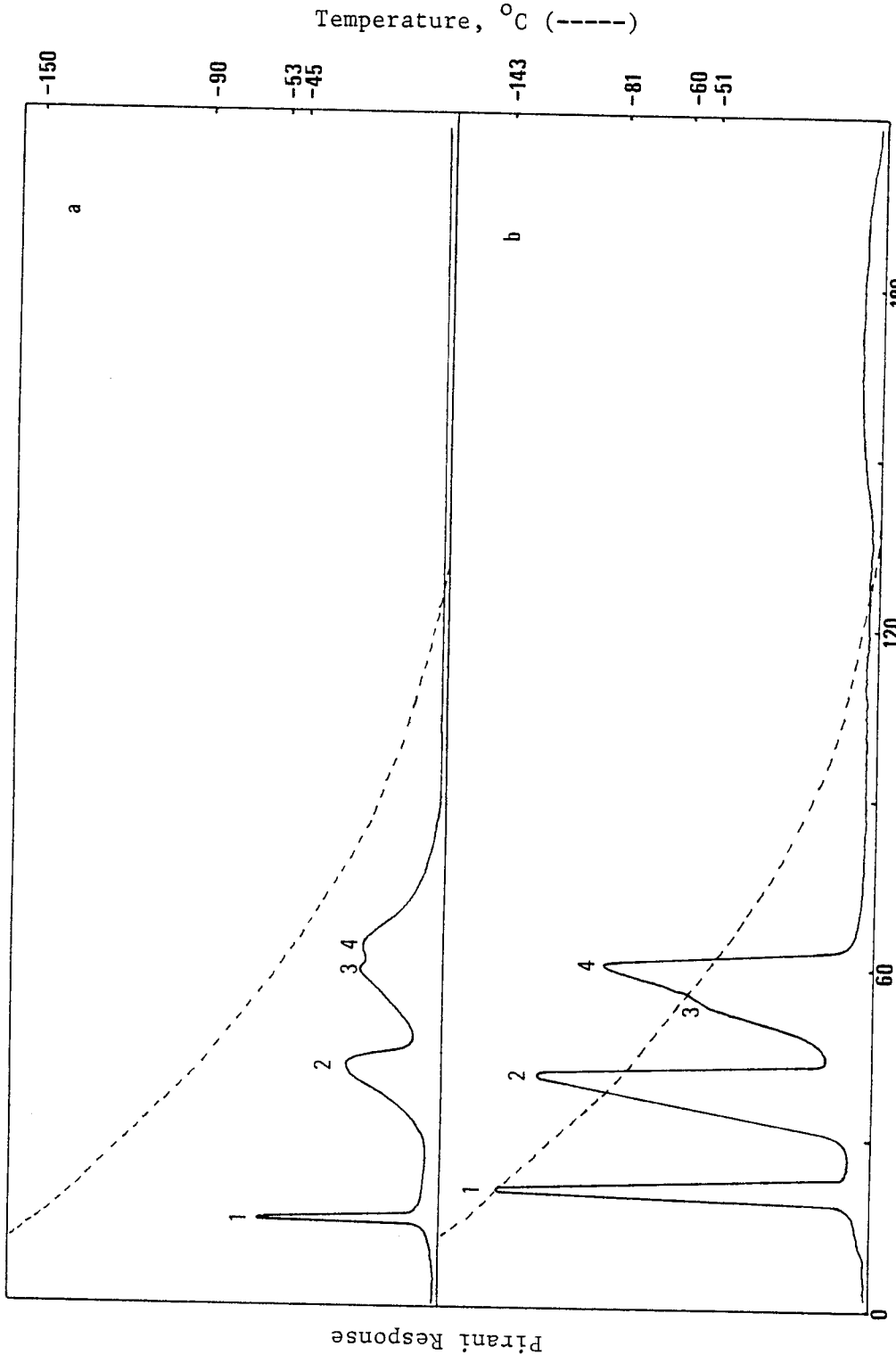
Condensable Products of Degradation

Analysis After Subambient Separation: The subambient distillation technique was used to separate mixtures of condensable products of degradation into smaller fractions to facilitate identification. Subambient traces which record the separated products from degradation of $P.U.1_{(0)}$, $P.U.1_{(11)}$, $P.U.1_{(44)}$ and $P.U.1_{(111)}$ are illustrated in Figure 6.V.

The infrared spectra of fractions 1, 2, 3 and 4 were sufficient to identify them as carbon dioxide, tetrahydrofuran, dihydrofuran and water respectively. Fractions 5 and 6 contained five compounds which were conveniently separated and characterised by G.C.M.S. Standard gas-liquid chromatographic procedure[66,67] proved the identity of four products to be aniline and p-toluidine (fraction 5) and N-phenylpyrrolidine and N-(p-tolyl)pyrrolidine (fraction 6) however a compound also present in fraction 5 with a parent ion mass, m/e = 121, was neither N,N-dimethylaniline nor p-aminobenzaldehyde[68] and remained unidentified. Figures 6.VI and 6.VII are typical gas-liquid chromatograms of fractions 5 and 6 after a subambient separation of degradation products from $P.U.1_{(44)}$.

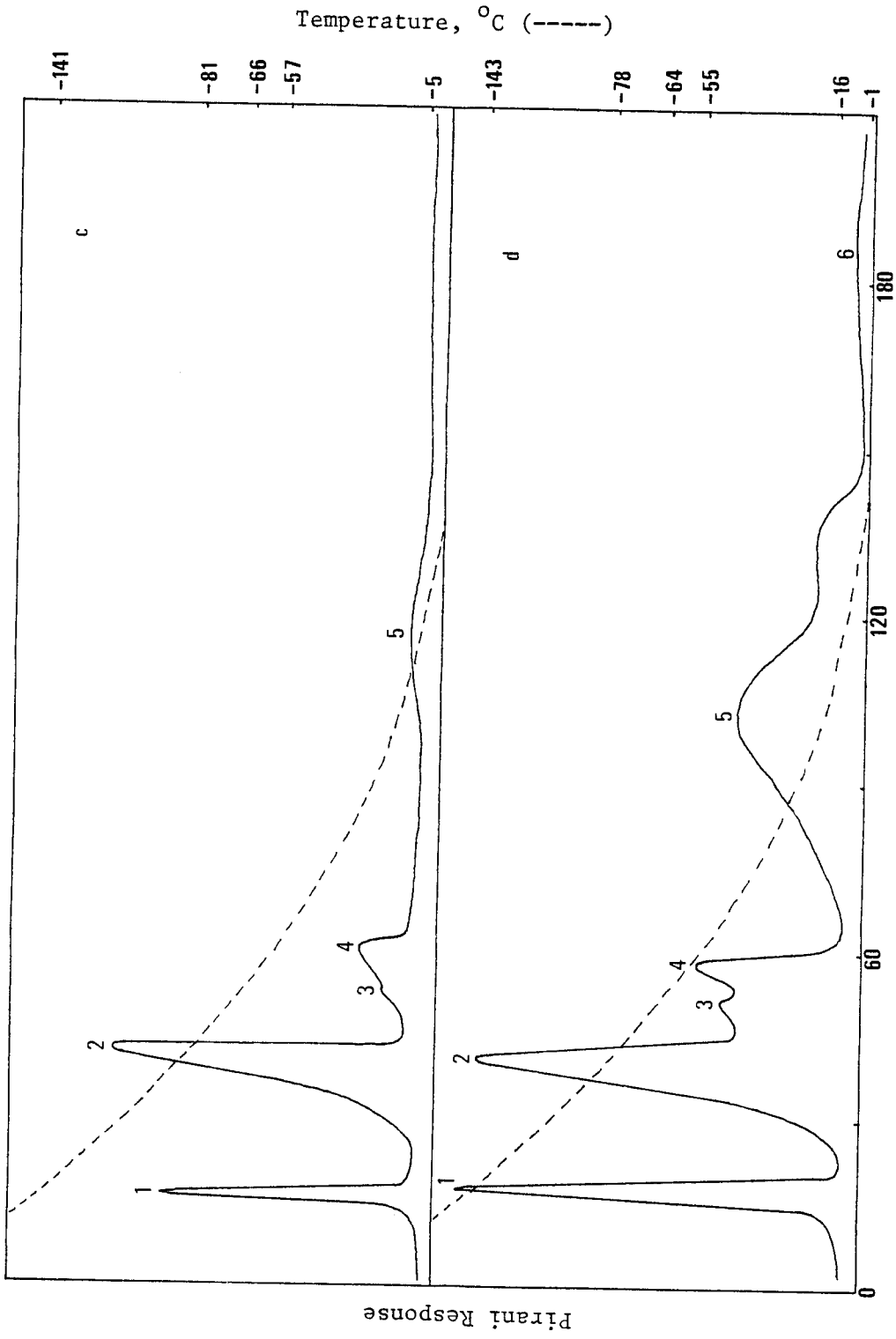
Quantitative Analysis of CO_2 and T.H.F.: Since the exact amount of carbon dioxide from thermal degradation of polyurethane can often be significant, quantitative measurements were made of carbon dioxide and tetrahydrofuran released by Polyurethane 1 during degradation.

Table 6.iii shows the number of moles of CO_2 and T.H.F. produced by 1g of Polyurethane 1 when it is heated to 500° under vacuum. Given that the urethane and butylene links in the polyurethane are the sources of CO_2 and T.H.F. respectively a theoretical yield has also been calculated. Graphs showing amount of product versus phosphorus content in



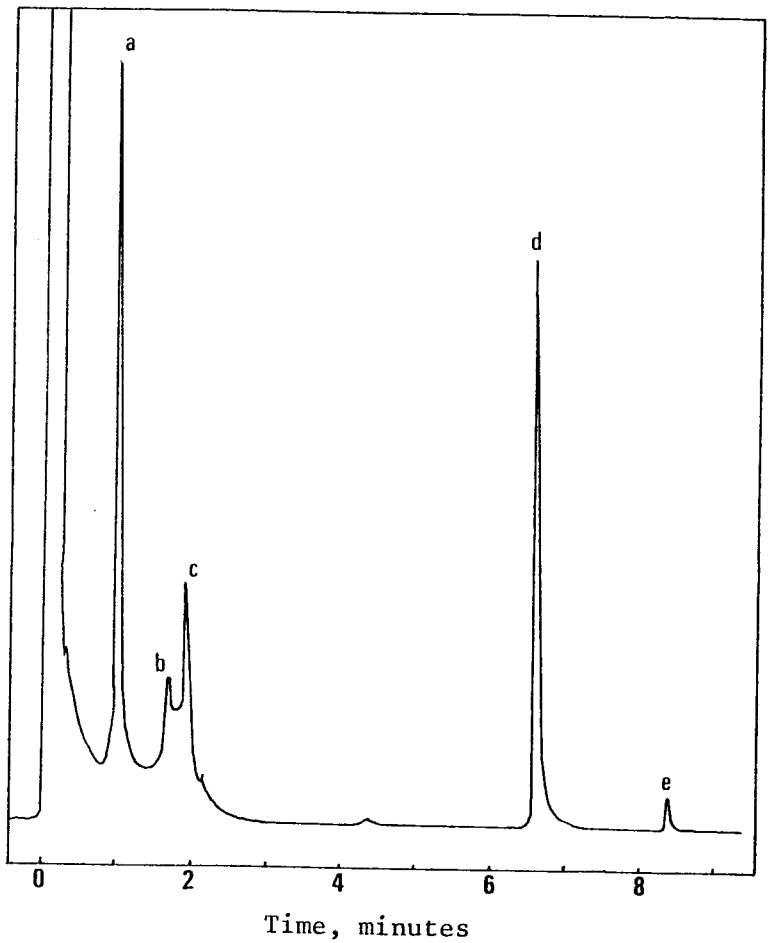
Subambient Traces: a = P.U.$^{1}_{(0)}$, b = P.U.$^{1}_{(11)}$

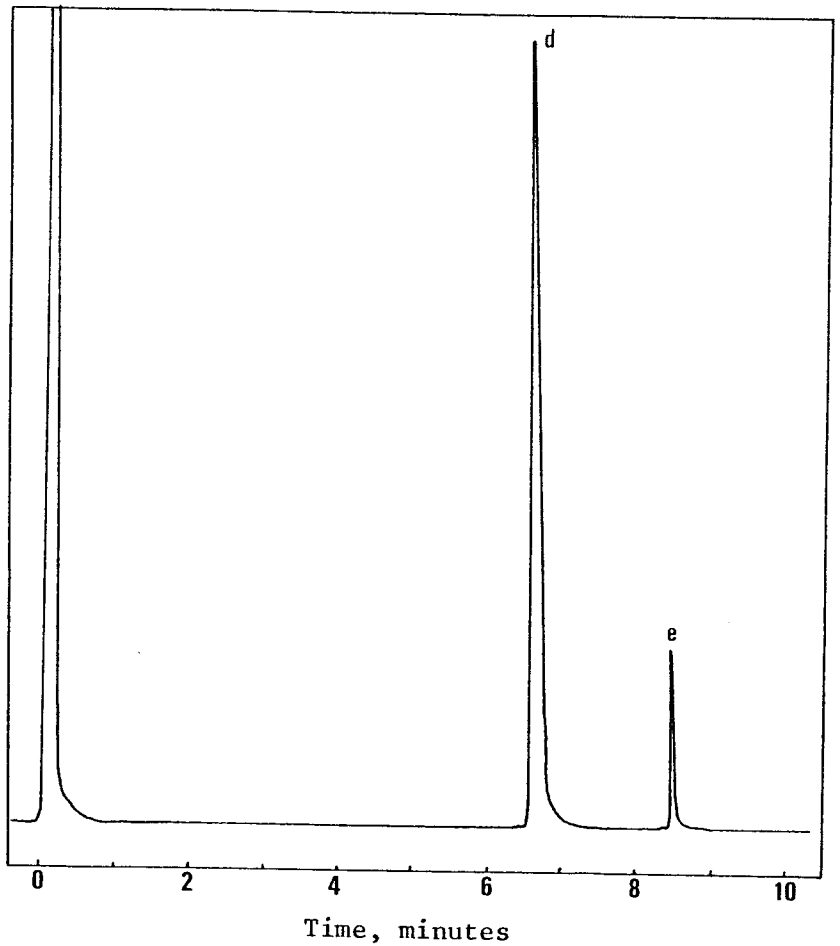
Figure 6.V(a),(b): Subambient Separation of Products from T.V. of Polyurethane 1



Subambient Traces: c = P.U.1$_{(44)}$, d = P.U.1$_{(111)}$

Figure 6.V(c),(d): Subambient Separation of Products from T.V. of Polyurethane 1





Identity and parent ion mass, m/e of peaks: a = Aniline, 93; b = Para-toluidine, 107; c = Unidentified, 121; d = N-phenylpyrrolidine, 147; e = N-(p-tolyl)pyrrolidine, 161

A 10', 1% OV-1 column separated the fractions during a programmed temperature rise of 10°/minute from 100°. The initial period was four minutes.

Figure 6.VI: Gas-Liquid Chromatogram of Subambient Fraction 5 Figure 6.VII: Gas-Liquid Chromatogram of Subambient Fraction 6

Table 6.iii: CO_2 and T.H.F. produced by Polyurethane 1

Polyurethane 1	Moles CO_2 from 1g P.U.1			Moles T.H.F. from 1g P.U.1		
	Theoretical	Found	% Yield	Theoretical	Found	% Yield
$P.U.1_{(0)}$	5.88×10^{-3}	7.03×10^{-4}	12.0	2.94×10^{-3}	1.95×10^{-4}	6.6
$P.U.1_{(11)}$	5.18×10^{-3}	1.15×10^{-3}	22.2	3.14×10^{-3}	9.13×10^{-4}	29.1
$P.U.1_{(22)}$	4.67×10^{-3}	1.54×10^{-3}	32.9	3.28×10^{-3}	1.28×10^{-3}	39.0
$P.U.1_{(44)}$	3.78×10^{-3}	1.88×10^{-3}	49.8	3.58×10^{-3}	1.29×10^{-3}	36.0
$P.U.1_{(54)}$	3.57×10^{-3}	2.37×10^{-3}	66.4	3.61×10^{-3}	1.15×10^{-3}	31.9
$P.U.1_{(111)}$	2.46×10^{-3}	2.58×10^{-3}	104.8	3.97×10^{-3}	6.19×10^{-4}	15.6

Polyurethane 1 have been drawn (Figures 6.VIII and 6.IX) to illustrate the effect of even small amounts of phosphorus.

Semi-Quantitative Analysis of Condensable Products: Inspection of the subambient traces from P.U.$1_{(0)}$ and P.U.$1_{(22)}$ reveals that peaks 5 and 6 are either too small for detection or totally absent. To determine if amines or pyrrolidines are produced by polyurethane containing a little phosphorus polyester the more sensitive technique, gas-liquid chromatography, was employed.

Thus the condensable products from thermal volatilisation of 100mg P.U.$1_{(0)}$ were collected, dissolved in 1.5ml analar ether and 0.7µl samples of solution injected into the chromatograph. The identical procedure was carried out with samples of all six polyurethanes and individual injections repeated twice. Two columns and operating temperatures were required to separate satisfactorily the condensables which were dissolved (see Chapter 2, page 27).

Peak heights of the same product in each chromatogram then indicated semi-quantitatively the relative abundance of that compound in each solution. An arbitrary scale, 0 to 5, has been assigned to describe the amount of one degradation product from each polyurethane. However the scale does not represent the true proportions of different degradation products from one polyurethane. Table 6.iv summarises the results of G.L.C. analysis. Traces of aniline and N-phenylpyrrolidine were among the degradation products of P.U.$1_{(0)}$.

Cold Ring Fractions

Six compounds volatile at degradation temperatures but involatile at ambient temperatures were detected after thermal degradation of Polyurethane 1. The amount of each material deposited on the walls of the T.V. tube varied according to the polyurethane studied. Since the tube was partially inserted in the oven (Chapter 2, page 19) its walls experienced a temperature gradient during the degradation process resulting in a crude separation of the fractions on their surface. Thus while some products condensed at the cold ring of the tube other less volatile fractions were found on the walls of the tube within the oven.

At the top of the T.V. tube a colourless liquid and white crystalline solid were identified spectroscopically as 1,4-butanediol and the cyclic diester butylene phenylphosphonate respectively. Further down the walls of the tube deposits of M.B.P.I. monomer and a polymeric solid were found. The polyurea synthesised from M.B.P.I. and 4,4'

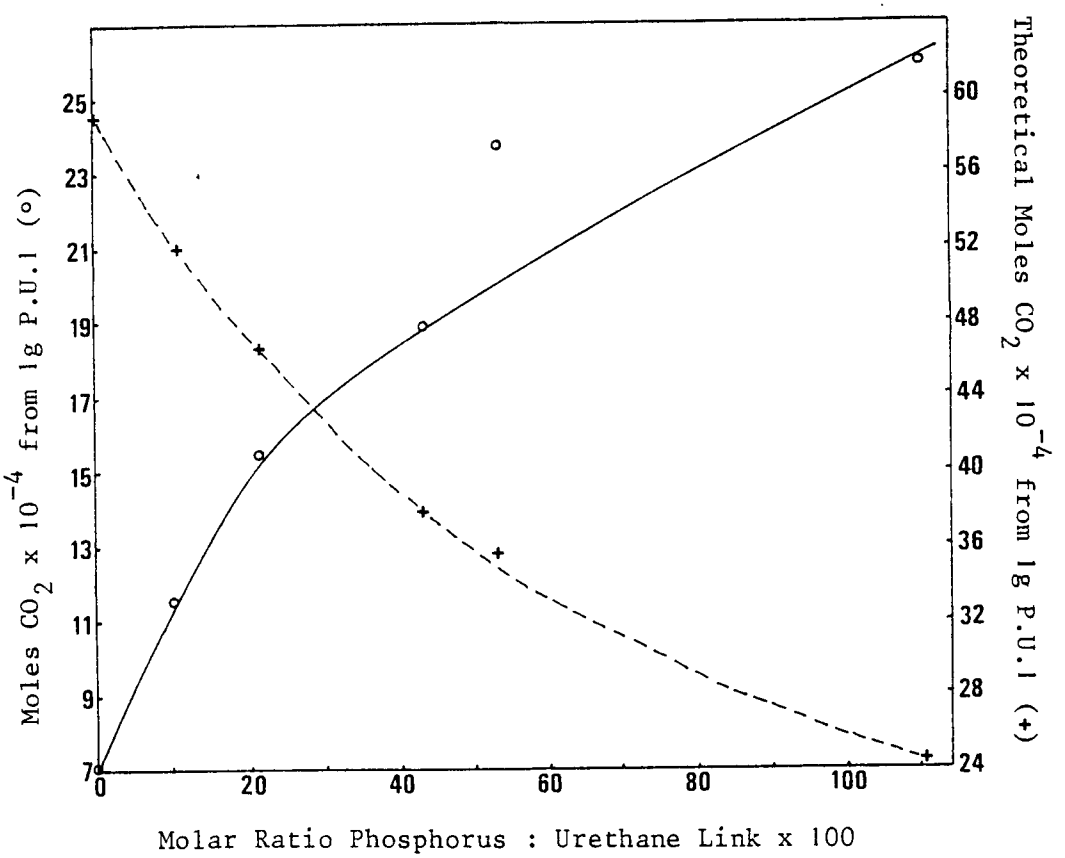


Figure 6.VIII: Graph of CO_2 versus Ratio Moles Phosphorus : Moles Urethane Links in Polyurethane 1

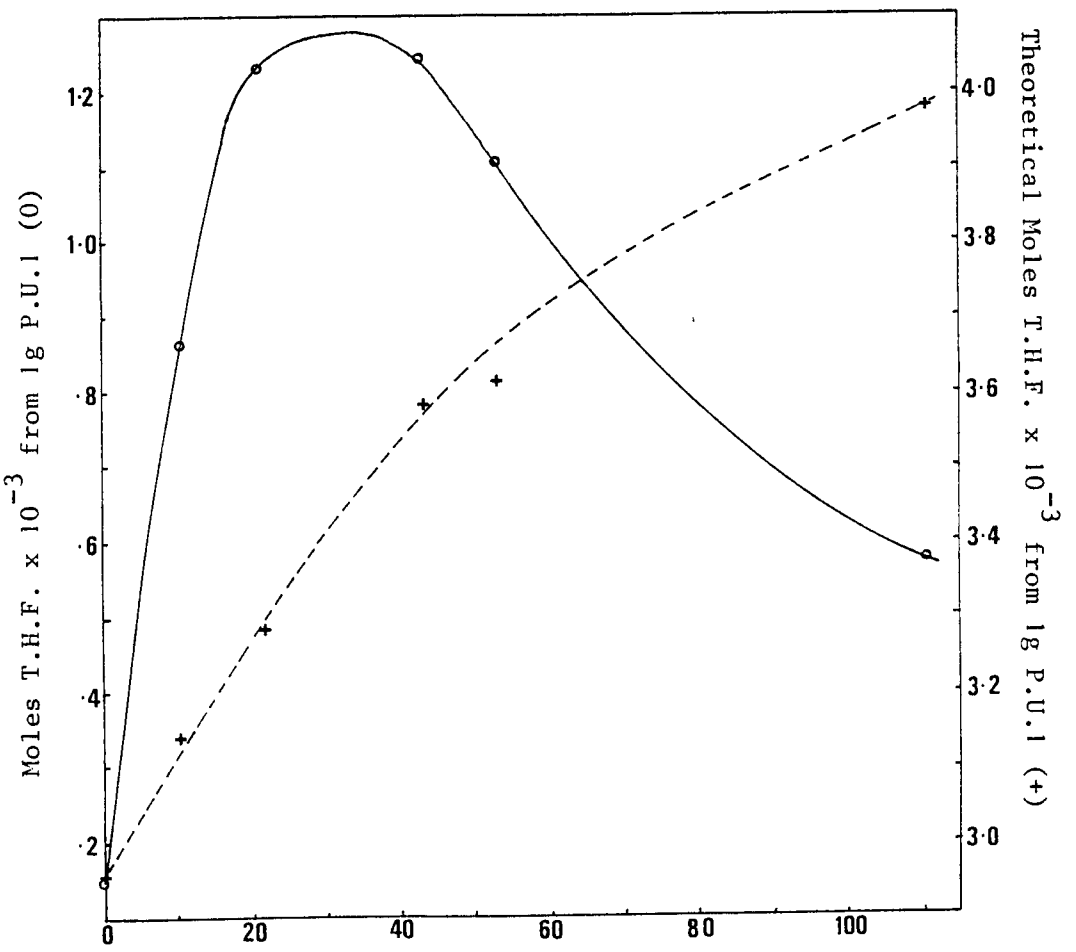
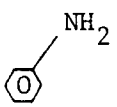
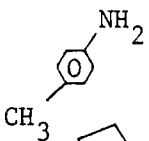
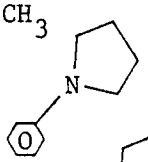
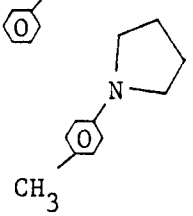


Figure 6.IX: Graph of T.H.F. versus Ratio Moles Phosphorus : Moles Urethane Links in Polyurethane 1

Table 6.iv: Relative Amounts of Individual Products from Different Polyurethanes

	P.U.1$_{(0)}$	P.U.1$_{(11)}$	P.U.1$_{(22)}$	P.U.1$_{(44)}$	P.U.1$_{(54)}$	P.U.1$_{(111)}$
T.H.F.	1	5	5	5	4	4
D.H.F.	1	1	2	1	2	1
H_2O*						
	1	4	4	4	4	3
	0	1	1	1	3	5
	1	1	1	2	3	5
	0	0	0	1	2	3

* Water was not recorded by G.L.C. equipped with a flame ionisation detector

methylenedianiline (M.D.A.) produced an I.R. spectrum identical to that recorded from the polymeric solid.

Significant amounts of a viscous cold ring fraction (C.R.F.X) were recovered from a large area inside the T.V. tube by adding a few drops of chloroform and allowing the product to dissolve. The solution was then removed and used to cast a thin film for I.R. analysis or studied by T.L.C.[69]. The I.R. spectrum of this cold ring fraction is drawn in Figure 6.X. C.R.F.X was found to contain some M.D.A. dissolved in a mixture of materials. However the infrared spectrum of M.D.A., shown in Figure 6.XI, clearly does not account for the intensity of absorption at 1510cm^{-1} in Figure 6.X. The following spectrum, Figure 6.XII, demonstrates that the amide structure prepared by the action of phenylphonic dichloride on 4,4' methylene dianiline also absorbs at that frequency and may be present to some degree. Thus a combination of thin layer chromatography and infrared spectroscopy indicated that the viscous fraction was 4,4' methylene dianiline dissolved in a mixture of oligomers which contained predominantly phosphonate and butylene segments but also primary amine groups and phosphonamide links.

The least volatile cold ring fraction in the T.V. tube appeared as a dark red, polymeric film insoluble in D.M.F., D.M.S.O. and arsenic trichloride. Brittle to touch, the film was produced in small amounts which restricted characterisation to infrared analysis and one micro-analysis. This final fraction (C.R.F.Y) contains 2.3% phosphorus by weight and its infrared spectrum is illustrated in Figure 6.XIII.

Clearly the material contains paradisubstituted benzene (815cm^{-1}) phosphorus-phenyl groups (1440, 1155 and 1000cm^{-1}) and N-H functions (3380cm^{-1}). The phosphonamide groups, $-\overset{O}{\overset{\|}{P}}-\overset{H}{\underset{|}{N}}-$ (1510cm^{-1}) may be present but no indication of urethane, urea or phosphonate ester, $-P-O-CH_2-$ is given. The absolute structure of C.R.F.Y has not been determined although evidence suggests it is largely polyamide with some cross-linking.

Residue

When heated to 500^{o} under vacuum, Polyurethane I leaves either a black or a light brown residue. Spectroscopic analysis of the black carbonaceous residue from P.U.I$_{(0)}$, P.U.I$_{(11)}$ and P.U.I$_{(111)}$ was impossible but infrared spectra were recorded of the residues left by the other polyurethanes. Results from residues from P.U.I$_{(22)}$, P.U.I$_{(44)}$ and P.U.I$_{(54)}$ were similar and a representative infrared spectrum is shown in Figure 6.XIV. The phosphorus content of each residue is given

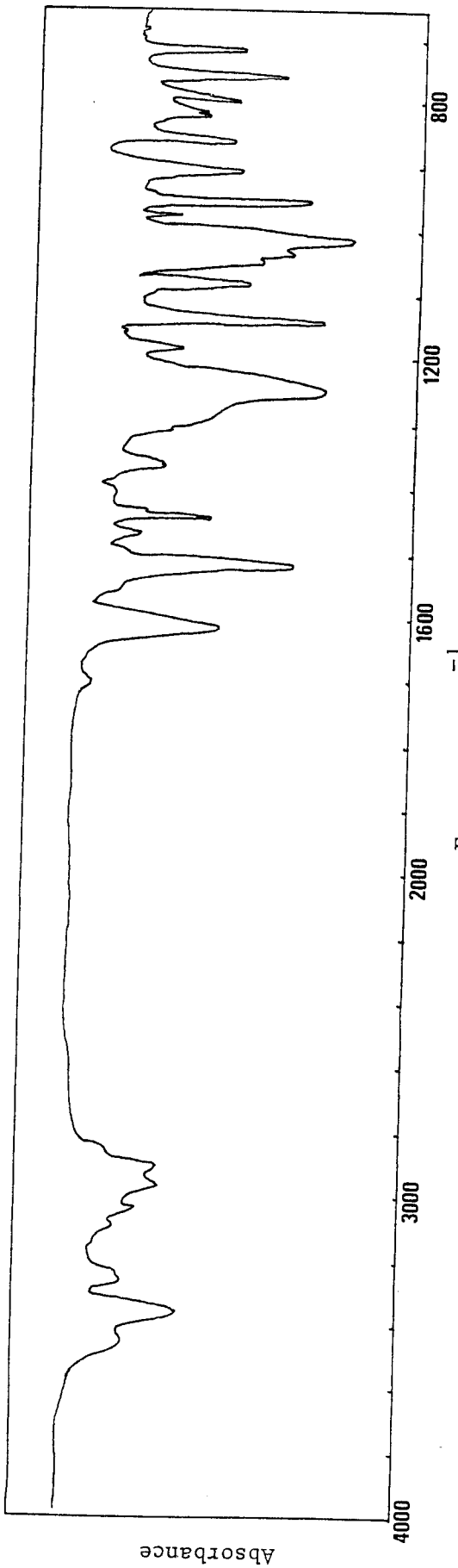


Figure 6.X: Infrared Spectrum of Cold Ring Fraction X

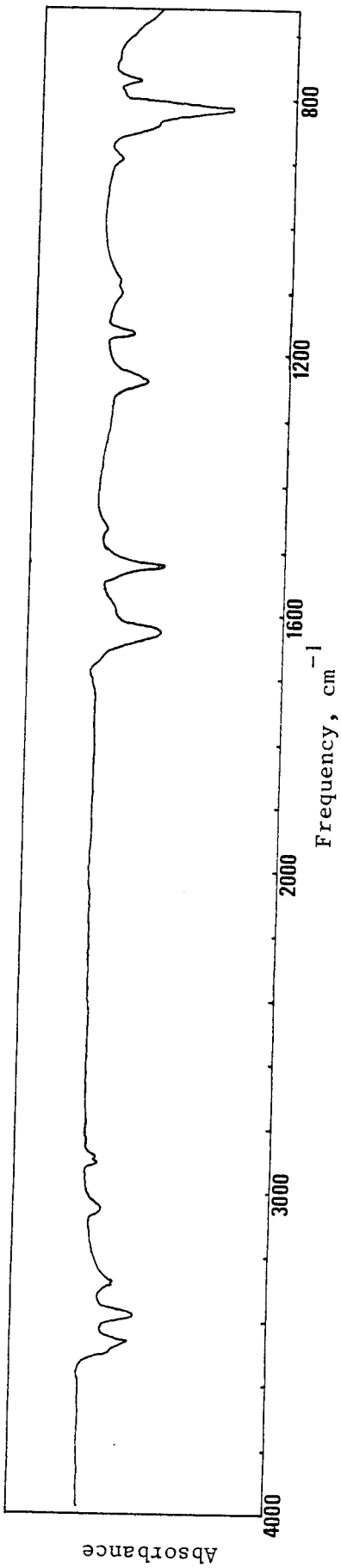


Figure 6.XI: Infrared Spectrum of 4,4' Methylene dianiline

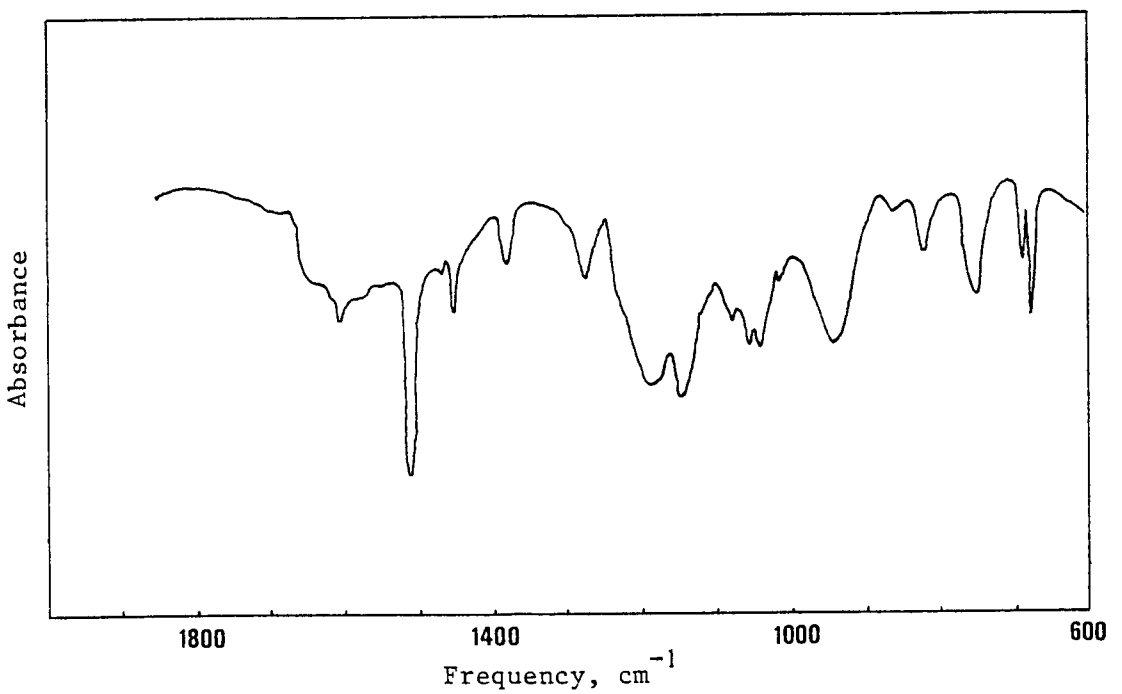
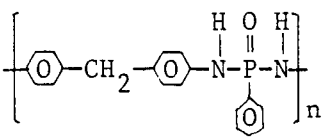


Figure 6.XII: Infrared Spectrum of Poly(phosphonylamide),



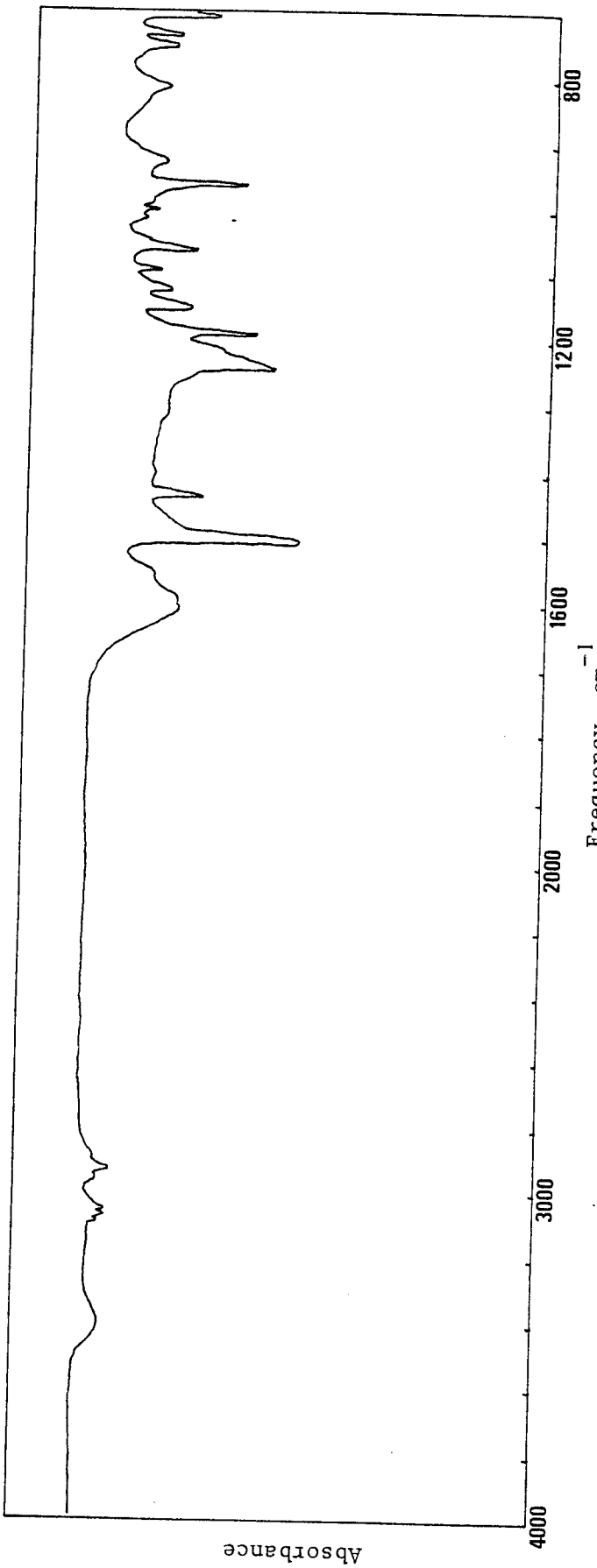


Figure 6.XIII: Infrared Spectrum of Cold Ring Fraction Y

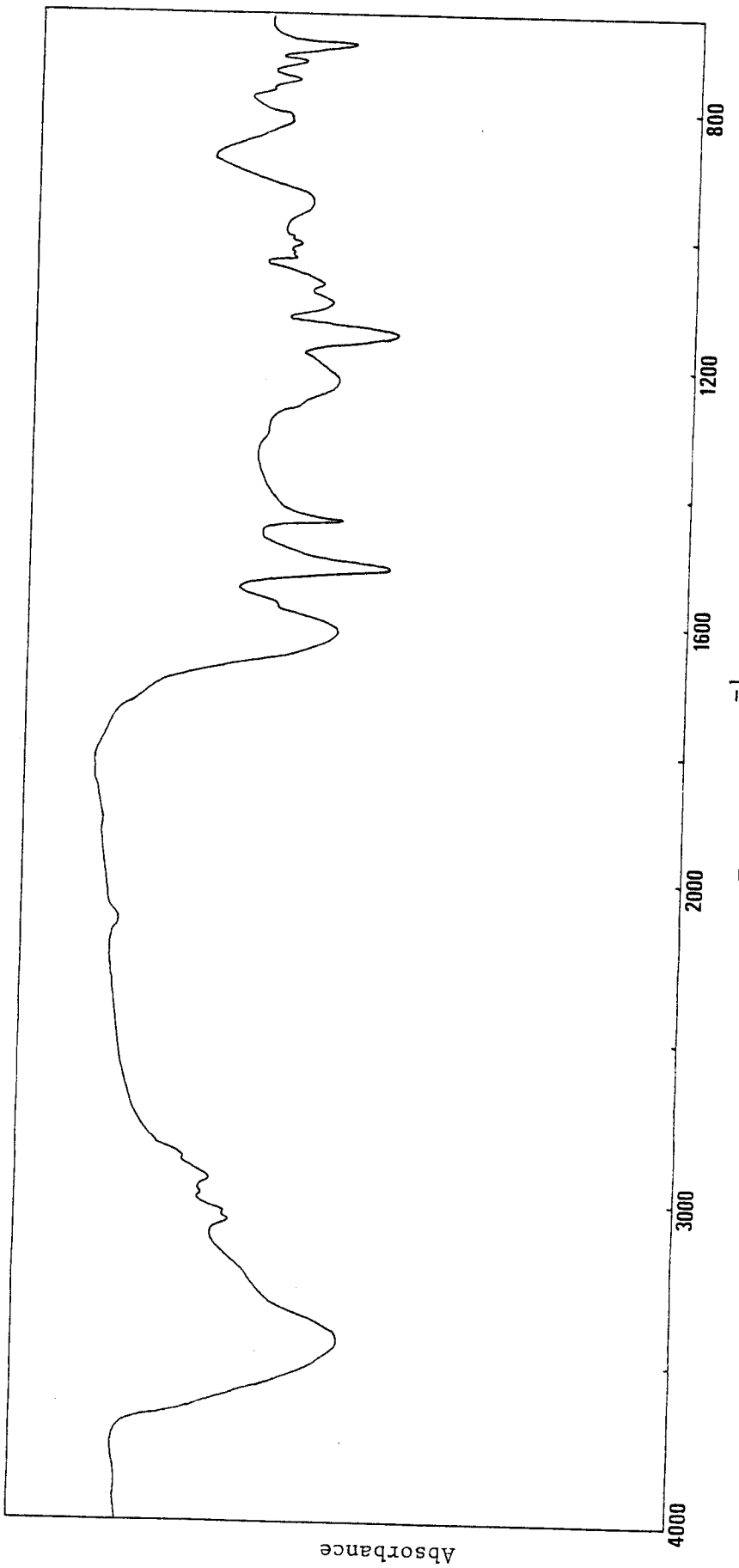


Figure 6.XIV: Infrared Spectrum of Residue from P.U.I.(22)

in Table 6.v.

Major I.R. absorptions at 1440, 1145, 1000, 750 and 699cm^{-1} show phosphorus-phenyl groups are present in large amounts. Phosphonyl, P = O (1220cm^{-1}) and condensed phosphonate links, P-O-P (945cm^{-1}) also exist but the strongest absorption is at 1510cm^{-1} and has been assigned tentatively to the N-H bend of amide segments.

So it appears the residue from P.U.1$_{(22)}$, P.U.1$_{(44)}$ and P.U.1$_{(54)}$, which is insoluble in common organic solvents, contains new bonds and a degree of crosslinking.

Intermediate Product

Infrared spectroscopy offers a convenient method of monitoring structural changes in a polymer as it is heated. Although thermal destruction is inevitable the production of transient species within the polyurethane lattice during a typical thermal degradation has been detected by this technique[16].

Thermal degradation of films of Polyurethane 1 was carried out using T.V. equipment and the programme interrupted when production of volatile material reached a maximum. I.R. analysis of the partially decomposed film revealed the presence of carbodiimide links with characteristic absorption at 2115cm^{-1}.

Figure 6.XV shows that although this absorption by partially degraded P.U.1$_{(0)}$ and P.U.1$_{(11)}$ is strong it is not discernable in the thermally modified P.U.1$_{(44)}$. Clearly the route to carbodiimide or the lifetime of the intermediate is affected by the presence of phosphorus.

Table of Products

Table 6.vi summarises the products from thermal degradation of Polyurethane 1 including the intermediate carbodiimide and indicates for each polyurethane which products were detected.

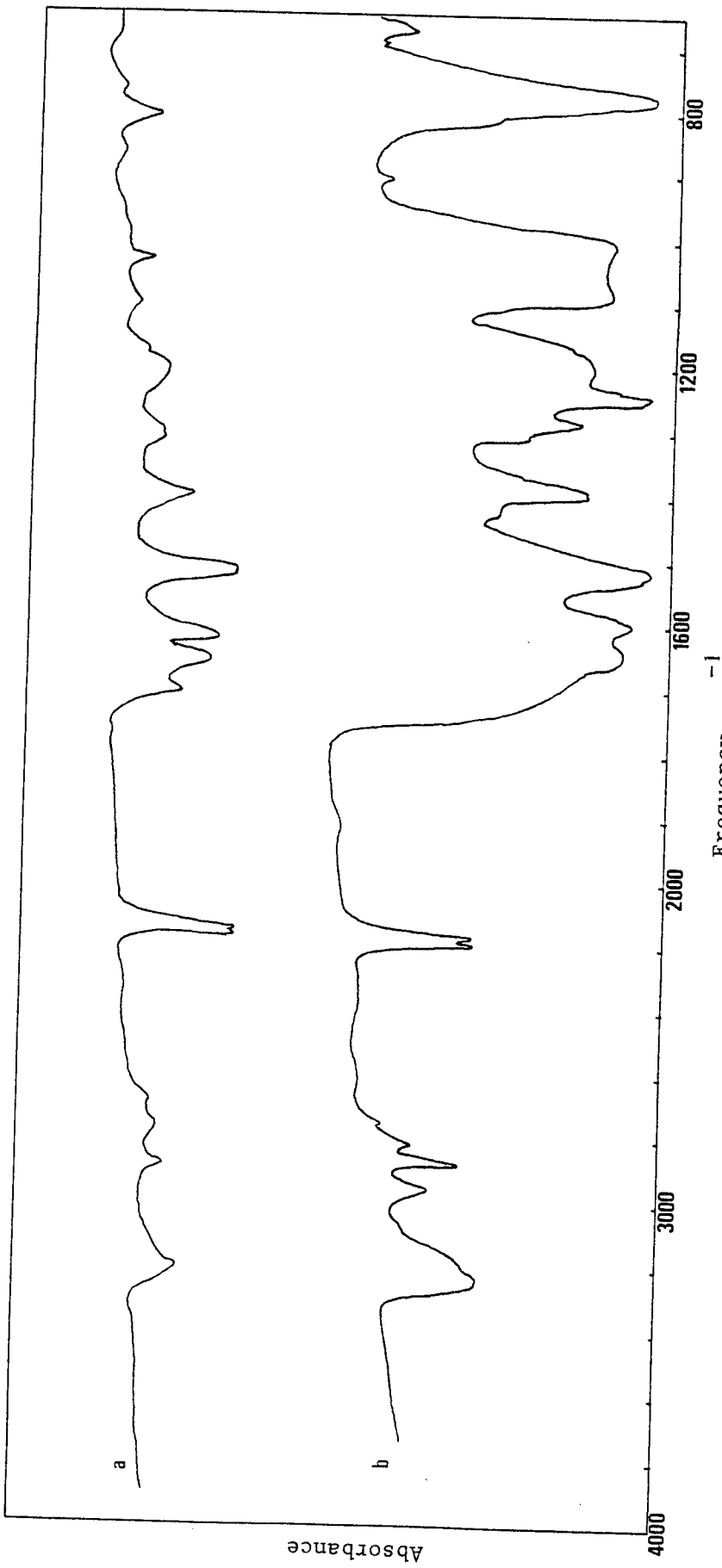
6.4 ISOTHERMAL DEGRADATION

The primary thermal decomposition of aromatic polyurethanes is reported to involve depolymerisation to monomer[70,71] and in the case of poly(butylene methylene bis(4-phenylcarbamate)) (P.U.1$_{(0)}$) this process is believed to be isolated at 210°[16]. That is changes in the infrared spectrum of P.U.1$_{(0)}$ maintained at 210° under continuous pumping are consistent with depolymerisation followed by volatilisation of monomer out of the polymer. Further isothermal degradation of Polyurethane 1 under vacuum was undertaken to detect any influence of

Table 6.v: Weight of Phosphorus (%) in Residue from Polyurethane 1

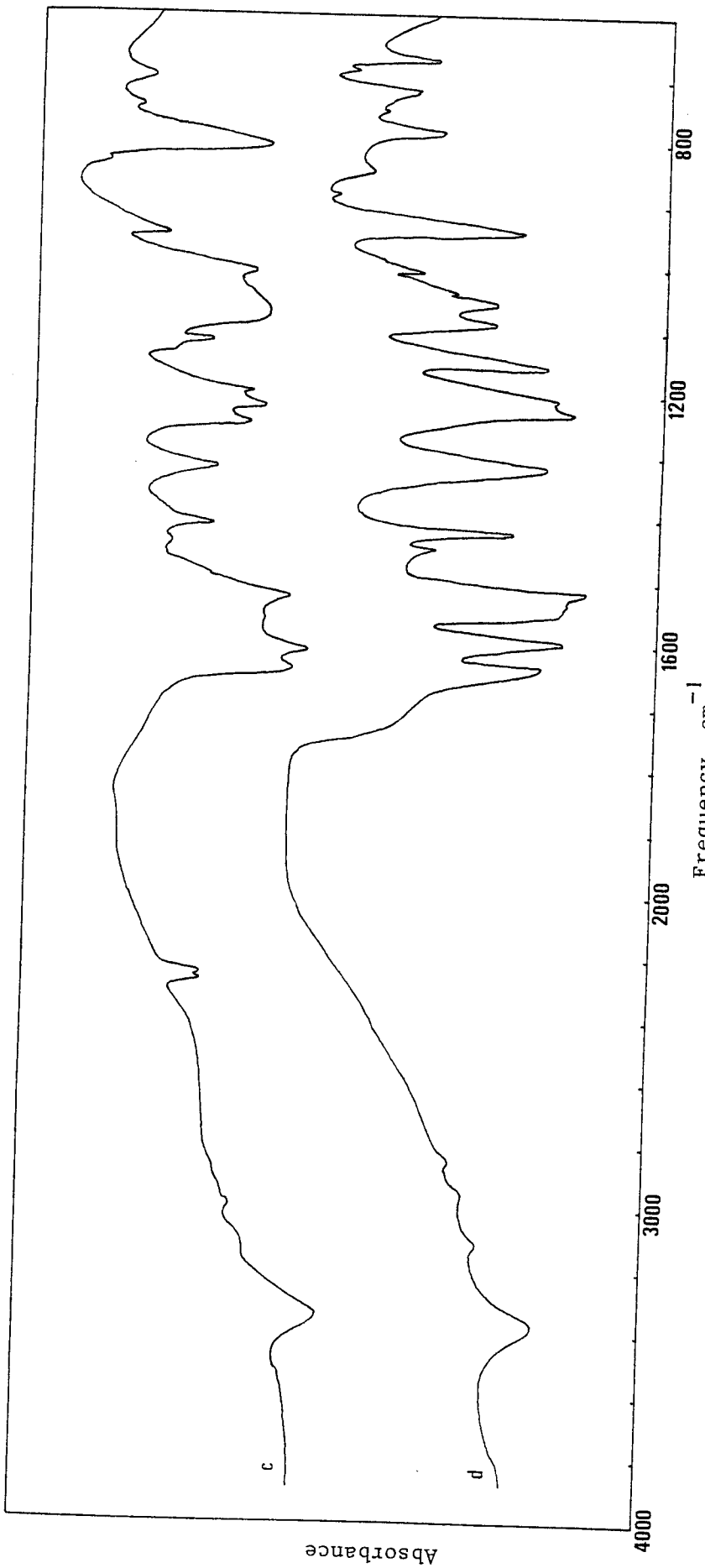
Polyurethane	Weight Phosphorus in Residue* (%)
$P.U.1_{(0)}$	0
$P.U.1_{(11)}$	2.28
$P.U.1_{(22)}$	4.75
$P.U.1_{(44)}$	8.22
$P.U.1_{(54)}$	9.40
$P.U.1_{(111)}$	11.32

* Residue after heating Polyurethane 1 at a rate of 10^{o}/minute from ambient temperature to 500^{o} under vacuum



I.R. Spectra: a = P.U.I$_{(0)}$, b = P.U.I$_{(11)}$

Figure 6XV(a),(b): Infrared Spectra of P.U.I$_{(0)}$ and P.U.I$_{(11)}$ Partially Degraded



I.R. Spectra: c = P.U.I$_{(22)}$, d = P.U.I$_{(44)}$

Figure 6.XV(c),(d): Infrared Spectra of P.U.I$_{(22)}$ and P.U.I$_{(44)}$ Partially Degraded

Table 6.vi: Table of Products from Thermal Degradation of Polyurethane 1

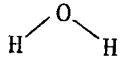
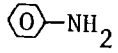
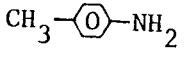
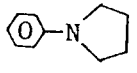
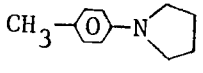
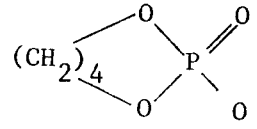
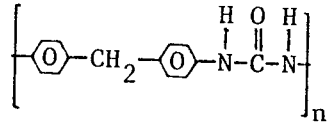
Product	Structure	P.U.1(0)	P.U.1(11)	P.U.1(22)	P.U.1(44)	P.U.1(54)	P.U.1(111)
Carbon dioxide	O = C = O	P	P	P	P	P	P
Tetrahydrofuran		P	P	P	P	P	P
Dihydrofuran		P	P	P	P	P	P
Water		P	P	P	P	P	P
Aniline		T	P	P	P	P	P
R-Toluidine		A	T	T	T	P	P
N-phenyl pyrrolidine		T	T	T	P	P	P
N-(p-tolyl)pyrrolidine		A	A	A	T	P	P

Table 6.vi (continued)

Cyclobutylenephenylphosphonate		A	A	T	P	P	P
1,4 Butenediol	$HO-CH_2CH_2CH_2CH_2OH$	P	T	A	A	A	A
Methylene bis(4-phenylisocyanate)	$OCN-\bigcirc-CH_2-\bigcirc-NCO$	P	P	P	A	A	A
4,4' Methylene dianiline	$H_2N-\bigcirc-CH_2-\bigcirc-NH_2$	A	A	T	P	P	P
Cold Ring Fraction X		A	A	P	P	P	P
Polyurea		A	P	P	P	P	A
Cold Ring Fraction Y		A	P	P	P	P	P
Carbodiimide	$-\bigcirc-N=C=N-\bigcirc-$	P	P	P	A	A	A
Residue		P	P	P	P	P	P

P = Present A = Absent T = Trace amounts

the polyester segment.

Figures 6.XVI and 6.XVII show respectively the infrared spectra of P.U.1$_{(22)}$ and P.U.1$_{(54)}$ heated isothermally in a vacuum for different durations. To augment the assignments in Table 4.i of Chapter 4, Table 6.vii was compiled from various references[4,9,10-14] to assist interpretation of the I.R. spectra.

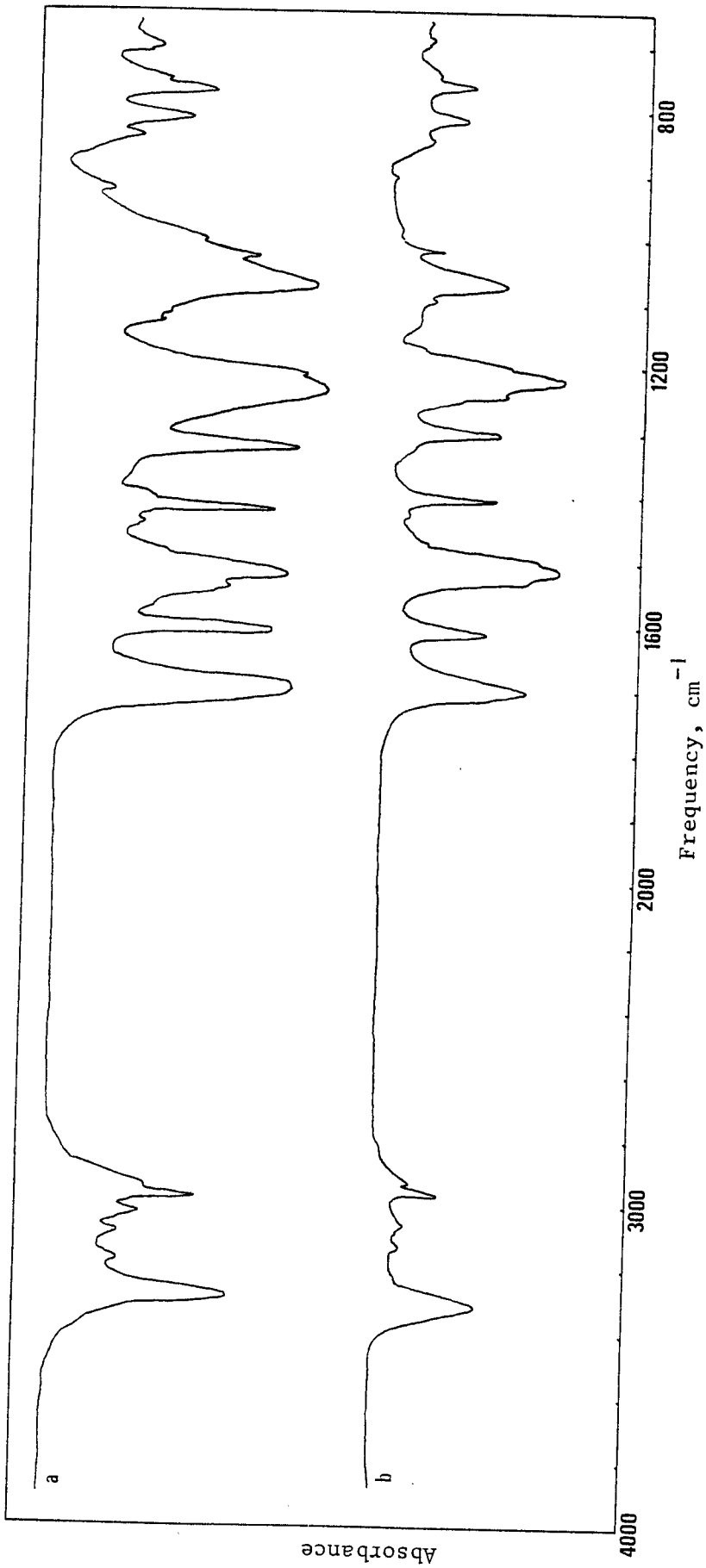
The spectrum of P.U.1$_{(22)}$ (Figure 6.XVI(a)) changes very little when the polymer is heated at 170° for 10 hours. However a decrease in the intensity of absorption at 1440, 1130 and around 1000cm^{-1} is observed, consistent with loss of polyester segment from the sample. When heated at 190° for 9½ hours (Figure 6.XVI(b)) the polyurethane suffers more extensive damage. I.R. analysis indicates bands at 1440, 1130 and 1000cm^{-1} are severely reduced and a significant amount of material has been lost.

Surprisingly an identical spectrum is recorded of P.U.1$_{(22)}$ which has been degraded at 210° for 10 hours and even after a <u>further</u> 12½ hours at this temperature very little change appears (Figure 6.XVI(c)). After a total of 324 hours at 210° (Figure 6.XVI(d)) the polyurethane appears as a pale brown, opaque solid and although phosphorus is still present (1440, 1130, 740 and 690cm^{-1}) the sample also contains urea (1650cm^{-1}).

The effect of heat on P.U.1$_{(54)}$ (Figure 6.XVII(a)) is more dramatic. Heating to 210° for one hour greatly reduces the infrared absorption of the polymer at 1440, 1130, ~1000, 746 and 692cm^{-1}. This early change is accompanied by volatilisation of the degradation product butylene phenylphosphonate (cyclic diester) out of the polymer to the cold ring. After 4 hours at 210° (Figure 6.XVII(b)) the polyurethane has lost much phosphonate and aliphatic C-H absorption but bands have appeared at 1640 and 1155cm^{-1} in its infrared spectrum. Thereafter amide I, II and III absorption in P.U.1$_{(54)}$ diminishes steadily (Figure 6.XVII(c)) however absorption by urea forming in the sample continues to increase until after 22½ hours the majority of carbonyl absorption appears at 1640cm^{-1} (Figure 6.XVII(d)). The infrared spectrum of P.U.1$_{(54)}$ after this treatment does not indicate the presence of allophanate, biuret or other isocyanate derivatives commonly found in polyurethane.

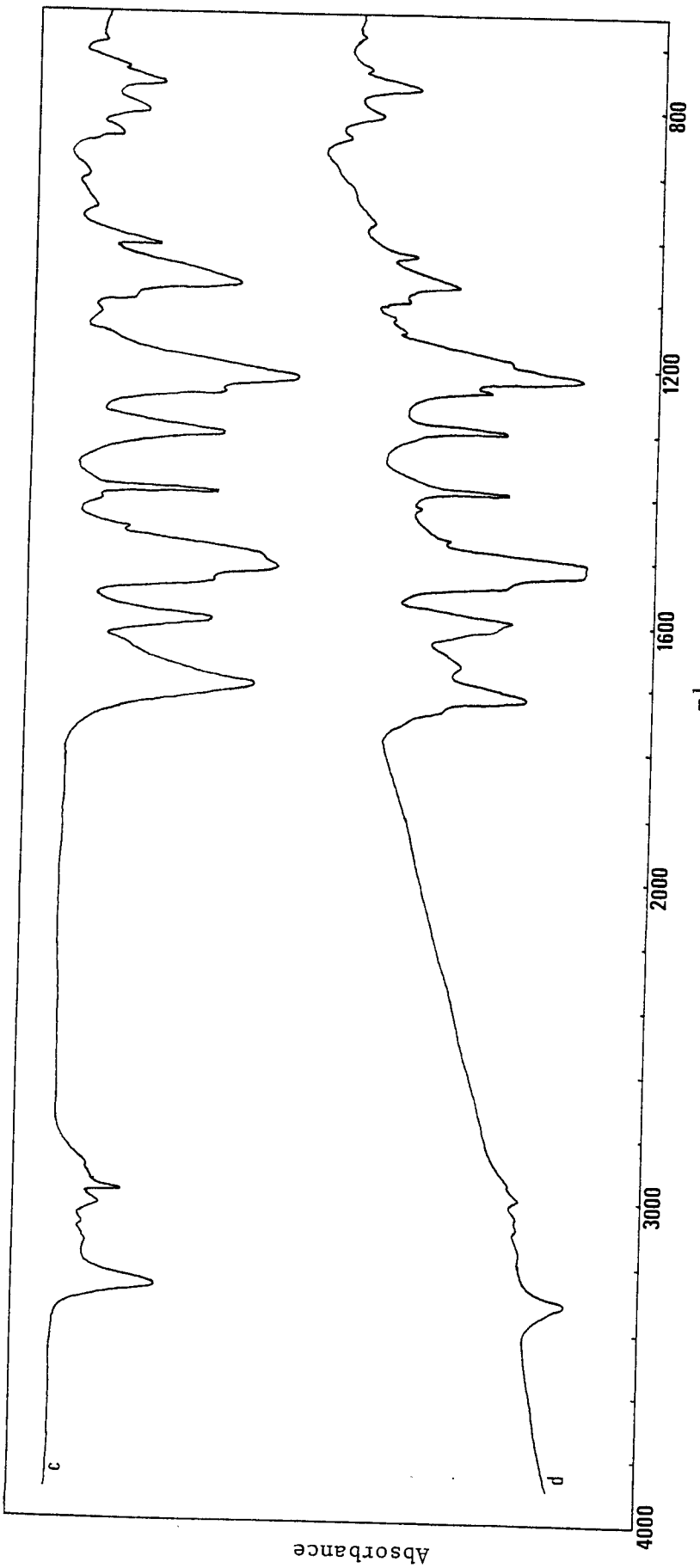
6.5 DISCUSSION AND CONCLUSIONS

The results from this chapter will be discussed in an effort to



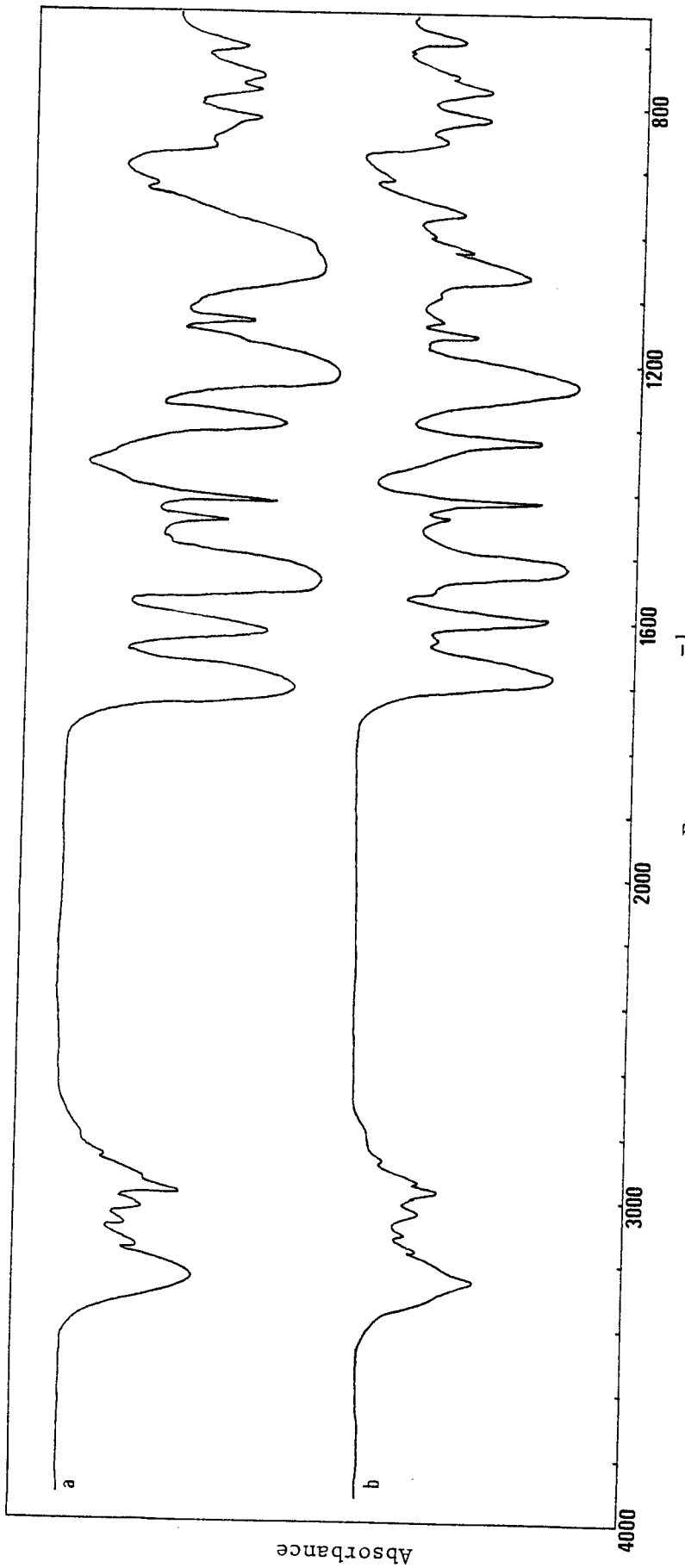
I.R. Spectra: a = P.U.1(22), b = P.U.1(22) after 9½ hours at 190°

Figure 6.XVI(a),(b): Infrared Spectra of Polyurethane 1 (22)



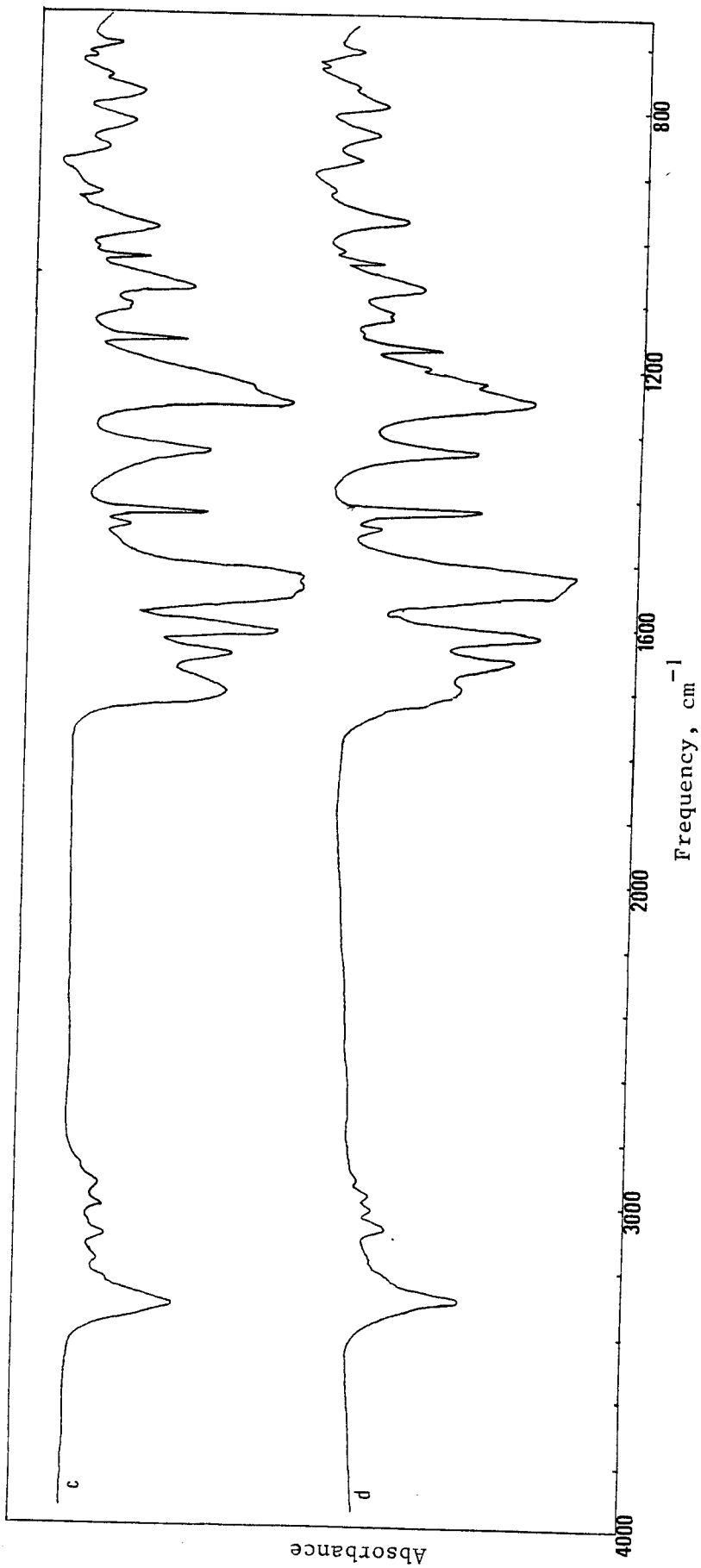
I.R. Spectra: c = P.U.1(22) after 22½ hours at 210°
d = P.U.1(22) after 324 hours at 210°

Figure 6.XVI(c),(d): Infrared Spectra of Polyurethane 1 (22)



I.R. Spectra: a = P.U.1$_{(54)}$, b = P.U.1$_{(54)}$ after 4 hours at 210°

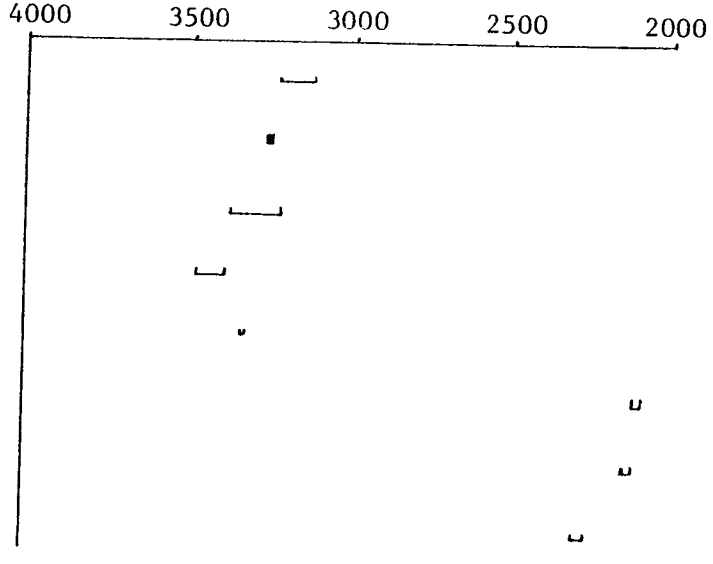
Figure 6.XVII(a),(b): Infrared Spectra of Polyurethane 1 (54)



I.R. Spectra: c = P.U.1(54) after 12 hours at 210°
d = P.U.1(54) after 22½ hours at 210°

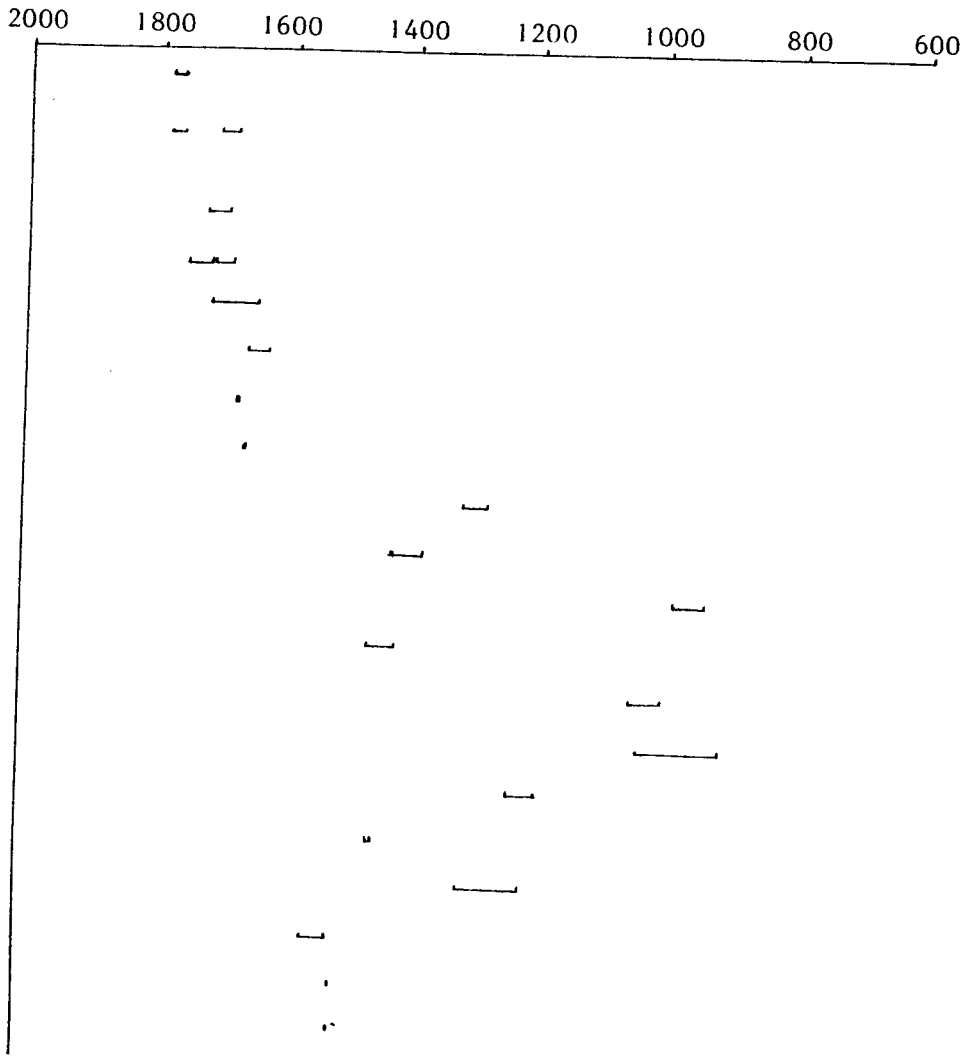
Figure 6.XVII(c),(d): Infrared Spectra of Polyurethane 1 (54)

Table 6.vii



3226-3115	ν	N-H in P(O)-N(H)-
~3250	ν	N-H in allophanates
~3400-3200	ν	N-H bonded
~3500-3400	ν	N-H free
3375-3350	ν	N-H in P^{III}-N(H)-
2217-2183		P-C ≡ N
2120		Carbodiimide -N = C = N-
2270-2240		Isocyanate -N = C = O

Table 6.vii (continued)



1770-1785 ν C=O of uretedinedione (isocyanate dimer)

1770-1780
1709-1689 ν C=O of isocyanurate (isocyanate trimer)

1739-1700 ν C=O in carbamates

1751-1721 and 1721-1695 ν C=O in allophanates

1720-1690 and 1708-1653 ν C=O in biurets

1670-1630 ν C=O in urea

~1681 ν C=N in carbodiimide dimer

~1669 ν C=N in carbodiimide trimer

1316-1275 ν C-N in P(O)-N(H)-C(Ar)

1425-1379 ν C=C in P(O)-N(H)-C = C(Ar)

971-922 ν P-N in P(O)-N(H)-Ar

1455-1420 ν P-Ar

1042-987 ν P-O-CH_2R

1025-900 P-O-P

1235-1192 ν P=O in R-O-P(O)(R)-N

1458-1445 ν P-O-⟨O⟩

1307-1206 ν P=O in -P(O)-O-P(O)

1560-1520 δN-H, Amide II

1510 Strongest Peak in Aldrich Compound

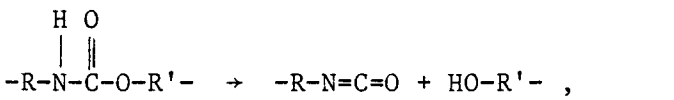
1510 Strongest Peak in polyamide synthesised

characterise the nature of thermal degradation of Polyurethane 1. However it may be relevant to mention firstly the types of mechanisms known to operate during thermal degradation of urethanes and polyurethanes.

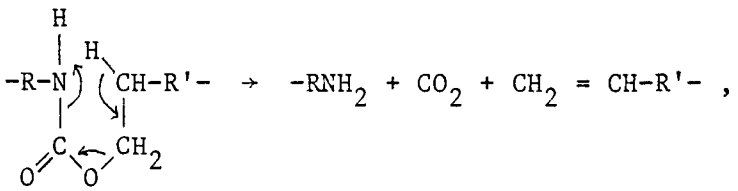
Review of Literature

Virtually every publication and review of thermal stability of polyurethanes agrees that the urethane link can degrade by three different mechanisms, namely:

(i) Depolymerisation to monomer:

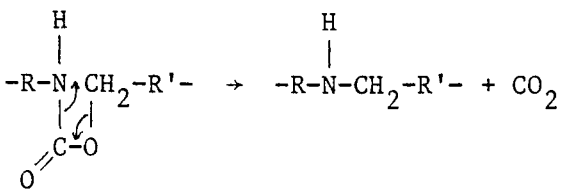


(ii) Decomposition by a concerted reaction to amine, olefin and carbon dioxide:



6 Membered Transition State

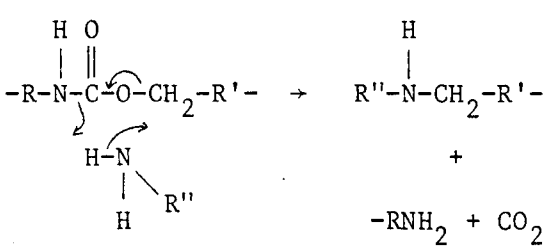
(iii) (a) Decomposition to secondary amine and carbon dioxide:



4 Membered Transition State

Mechanism (iii)(a) may not be strictly accurate since a detailed kinetic study of the decomposition of the model 1-phenylethyl phenylcarbamate indicated the process was bimolecular[78]. The mechanism proposed by Dyer and Wright involves a primary amine, namely

(iii) (b)



Matuszak and Frisch[44] have presented evidence which concludes mechanism (i) is the degradation process favoured by urethanes from cycloaliphatic isocyanates whereas urethanes from aromatic isocyanates decompose predominantly to amine, carbon dioxide and olefin. This is a poor generalisation. It is more accurate to say the mode of decomposition is a function of isocyanate and alcohol precursor[78,79], the nature of heating[80,81], the atmosphere[82] and even the preparative history of the urethane[83].

Mechanism (i) of Thermal Degradation of Urethane: In fact a literature survey indicated that heating the majority of carbamates (urethanes), biscarbamates and polyurethanes based on aromatic isocyanates regenerates isocyanate and alcohol in high yield[71,78,79,84-86].

Particularly relevant to this work are reports by Grassie and Zulfiqar[16] who showed P.U.I$_{(0)}$ degrades under vacuum at 210° purely by mechanism (i) and Ballistreris et al.[81] who decomposed the same polymer quantitatively to M.B.P.I. and B.D.

Mechanism (ii) of Thermal Degradation of Urethane: In contrast the products of degradation associated with mechanism (ii) that is olefin, amine and CO_2 are generally detected in low yields[16,78,84-86] from urethanes prepared from aromatic isocyanates. Exceptions do occur[44,78,81] notably N-substituted urethanes which cannot form isocyanate. For example, ethylcarbazole-9-carboxylate produces only amine, carbon dioxide and ethylene if heated[78].

Mechanism (iii) of Thermal Degradation of Urethane: This mechanism is believed to operate during thermal degradation of urethanes when secondary amines are detected as products. This has been observed among model urethanes[78,79,87] but only Dyer and Dunbar[65] have published evidence that the process occurs in polyurethanes. The polymers were "Phosphorus Containing Polyurethanes" which liberated almost quantitatively carbon dioxide without the simultaneous production of olefin or carbodiimide.

In special cases, therefore, and under specific conditions it appears that each mechanism of degradation can operate exclusively. However the initial degradation of polyurethane is generally a combination of these processes. Products from the thermal degradation of urethane, other than those mentioned, are accounted for by "secondary reactions"[17,71,79,86,88] when the products of primary degradation reside in the hot polyurethane long enough to react.

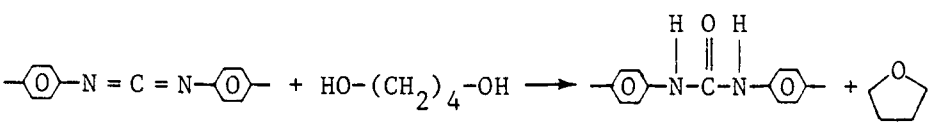
So while ethanol can be extracted continuously during thermal degradation of ethyl carbanilate to leave phenylisocyanate[78], the escape of primary products from a commercial polyurethane foam as it decomposes is less facile. The products detained in the hot cross-linked polymer matrix often undergo secondary reaction to a wide range of materials[80,88].

Discussion of Results

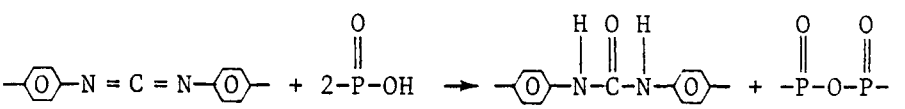
T.V.A.: The general appearance of curves produced by thermal volatilisation of Polyurethane I has been explained by the quantities of volatile products CO_2 and T.H.F. However higher boiling condensables indicated by the subambient distillation technique allow a more detailed interpretation. D.H.F. and water produced by each member of the polyurethane series pass through the 0 and -45^{o} traps in the T.V. system but are condensed at lower temperatures. When these volatile products are present the -45 and -75^{o} traces on the T.V. curve will not be coincident. Aniline, which condenses below 0^{o}, is responsible for the separation of the 0 and -45^{o} traces on the thermogram. On the T.V. curve of $P.U.I_{(III)}$ between polymer temperatures 250 and 300^{o} this separation is considerable and is ratified by the quantity of aniline recorded in the corresponding subambient trace.

Intermediate: Of the new chemical bonds formed by Polyurethane I during thermal degradation, all but carbodiimide were intact, either among cold ring fractions or residue, at 500^{o}. Carbodiimide, the condensation product of two isocyanate functions, is lost from the system at higher temperatures through either further degradation to a carbonaceous residue or reaction to a variety of products. Possible reactions include dehydration of alcohols[16] and of phosphonic acid functions[89]:

(iv)

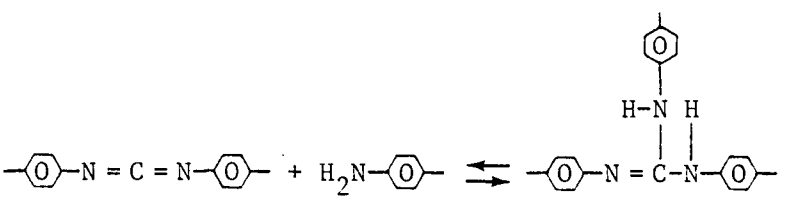


(v)



All structures in (iv) and (v) have been identified in this work. Carbodiimide can also react with amines:

(vi)



Although guanidine structures were not identified in P.U.1 as it degraded the reversible reaction may nevertheless operate.

The generation of carbodiimide intermediate structures in P.U.1 is clearly retarded when phosphorus is present (Figure 6.XV) and this is explained by the relative rates of reaction of isocyanate with amine and isocyanate self-condensation. Since phosphorus encourages production of large quantities of amine by P.U.1 free isocyanate from primary degradation will react to form urea more readily than carbodiimide. The transient nature of the C.D.I. structure during thermal degradation and its suppression by concentrations of amines[17] have been encountered previously[10,16,71,86].

Residue: Infrared spectroscopy and microanalysishave shown phosphorus is present in the cold ring which contradicts claims made by Papa and Proops[15] that the phosphorus of flame retardants is totally retained in the residue of polyurethane after isothermal degradation in air. Their method of degradation, called charring, was repeated for P.U.1 and phosphorus contents measured. The results which again disagree with Papa are shown in Table 6.viii. At no time can microanalysis of residue or char account for all the phosphorus which was present in the original polyurethane. These findings are similar to results published by Backus et al.[82] who even detected phosphorus among volatile products of degradation. It would seem the combination of polyurethane, chemical form of the phosphorus and the nature of pyrolysis influences the amount of phosphorus retained in the polymer matrix during and after thermal degradation.

Quantitative Carbon Dioxide Measurement: Quantitative gas analysis confirmed the qualitative evidence from T.V.A. that polyurethane containing copolymerised phosphorus liberates far more CO_2 and T.H.F. during thermal degradation than its phosphorus-free counterpart, $P.U.1_{(0)}$. The yield of CO_2 from $P.U.1_{(111)}$ can be explained not by questioning the quantity of gas recovered after degradation but the theoretical yield from which the percentage value was calculated. A small molar excess of free diisocyanate was always used during polymerisation[41,70] and, by molecular weight and phosphorus abundance, has proved more reactive. Since a concentration of urethane links greater than calculated exists in each polyurethane quantities of CO_2 larger than expected may be produced.

Cold Ring Fraction: The combination of T.G. and T.V.A. has indicated most of the products of degradation which are volatile at degradation

Table 6.viii: Phosphorus Content of Residue and Char as a Percentage of Phosphorus present initially in Polyurethane 1

Polyurethane	Weight of Phosphorus in Polyurethane (%)	Residue after T.V.A.* / Weight of Phosphorus in Residue (%)	Fraction of Original Phosphorus still Present (%)	Char after Isothermal** / Weight of Phosphorus in Char (%)	Fraction of Original Phosphorus still Present (%)
P.U.1$_{(0)}$	0	0	-	0	-
P.U.1$_{(11)}$	1.48	2.28	5.2	1.53	45.3
P.U.1$_{(22)}$	2.49	4.75	5.3	4.02	39.8
P.U.1$_{(44)}$	3.74	8.22	15.6	4.52	39.3
P.U.1$_{(54)}$	3.76	9.40	21.2	7.15	39.6
P.U.1$_{(111)}$	6.36	11.32	24.4	11.05	45.0

* Programmed heating at a rate of 10°/minute to 500° under vacuum

** Heating at 300° for 45 minutes under air

temperatures but involatile at ambient temperatures are evolved by Polyurethane 1 at elevated temperatures late in the degradation process. Polyurea is the most abundant compound of this type, collected at the cold ring of the T.V. tube. To identify the source of this polymer found at the cold ring, two blends of phenylphosphonic acid (P.P.A.) namely carbodiimide with P.P.A. and M.B.P.I. with P.P.A. and the polyurea itself were degraded under identical T.V.A. conditions.

Only polyurea volatilised when heated and redeposited unaltered on the cooler parts of the T.V. tube. It appears that polyurea formed during thermal degradation of P.U.1 escapes intact from the degradation zone and is not a result of reaction between any two of the aforementioned compounds.

Isothermal Degradation: The thermal degradation of polyurea prepared from phenylphosphonic dichloride and various diamines commences with loss of phosphorus-phenyl (P—⬡) structures. Evidence of this from I.R. spectroscopy was collected by Carraher and Krueger[64] who may have misinterpreted the effect as consistent with rupture of the phosphorus-phenyl bond. This bond is known to be very stable[90], exists in polyurethane residues under vacuum at 500° and is unlikely to break in polyureas at ~300°. Therefore it seems that initial loss of small volatile derivatives of phenylphosphonic acid from the backbone of polymers as they are heated is not unique.

Improvement of thermal stability of polyurethanes by incorporating small amounts of urea in the backbone has been reported[44]. This may explain why isothermal degradation of $P.U.1_{(22)}$ at 190° is inhibited after nine hours. Urea clearly exists in the modified polymer at this stage and further treatment at that temperature must be sustained for long periods before deterioration continues.

Features of Thermal Degradation of Polyurethane 1: Since carbodiimide was shown to be instrumental in formation of dihydrofuran from 1,4-butanediol[16] an alternative route to the volatile product of degradation from $P.U.1_{(44)}$, $P.U.1_{(54)}$ and $P.U.1_{(111)}$ must exist. Given that the phosphorus polyester segments degrade initially in a manner similar to its polyol precursor, phenylphosphonic acid functions should be generated during thermal degradation of P.U.1. Thus phenylphosphonic acid was prepared from P.P.D. and water, recrystallised and reacted in equimolar proportions with 1,4-butanediol in a sealed evacuated system. Analysis of products after heating at 250° for 30 minutes indicated large quantities of T.H.F. and D.H.F. Clearly more than one route

exists to produce dihydrofuran from the butylene segments in Polyurethane 1.

Many of the characteristics of P.U.1 have been recorded by previous workers. Phosphorus polymers of very high molecular weight are uncommon and polyurethanes containing phosphorus which have molecular weight as low as ~1000 have been studied[65]. Polyurethane $1_{(0)}$ is a white solid but as amounts of copolymerised phosphorus polyester are increased the polymer assumes a noticeable yellow colour. This appearance is common among polyurethanes which contain phosphorus.

The influence of phosphorus on the temperature of initial loss of weight from P.U.1 is clearly shown by T.G. and is observed among polyurethanes which contain commercial phosphorus flame retardant additives[82,91].

The volatile products of degradation from Polyurethane 1, CO_2, T.H.F., D.H.F., water and amines are characteristic of urethane decomposition[10,79,92]. Monomer and M.D.A. have also been produced from the thermal breakdown of polyurethane prepared from M.B.P.I.[71,86]. Grassie and Zulfiqar[10] remarked that the quantity of volatile products from thermal degradation of P.U.1 increase dramatically when phosphorus is present which they suggested was a manifestation of catalytic influence by phosphorus on the normal degradation process. This work has confirmed quantitatively the profound effect of copolymerised phosphorus on the generation of volatile material by polyurethane and by the significant absence of acid functions among products of degradation reflects the theory that phosphorus operates as an acid to modify the mechanism of thermal degradation.

It seems with so much correlative evidence that Polyurethane 1 behaves in a way common to that class of polymer and although no reports were found describing the species formed by interaction of phosphorus with urethane during thermal degradation they too may be reproduced in different systems of urethane and phosphorus copolymer.

Summary of Thermal Degradation of Polyurethane 1: With the evidence in this chapter and a little knowledge of thermal degradation of polyurethanes it is possible to describe broadly the types of rearrangement undergone by Polyurethane 1 as it is heated in absence of air.

The first sign of instability in the polyurethane appears among the phosphorus polyester segments from around 170° when some phosphorus volatilises out of the polymer as the cyclic diester, butylene phenyl-

phosphonate. Full thermal degradation, probably promoted by acid functions appearing in the ester regions, follows rapidly thereafter although when high concentrations of phosphorus are present simple depolymerisation is not the dominant mechanism.

Initial degradation is endothermic although the appearance of amine in the polymer which then reacts rapidly with isocyanate may be responsible for a sudden release of heat and thereby accelerate decomposition. Until ~280° the degradation process is characterised by evolution of volatile secondary products in particular T.H.F. and D.H.F. These are created in high yield from 1,4-butanediol when phosphoric or phosphonic acids are present[93]. Other volatile products of degradation include amines, some of which react with isocyanate as it is continually produced thereby reducing the amount of carbodiimide formed at higher temperatures (~300°).

At ~350° heat is no longer required from the surroundings to support degradation of the material which at this stage weighs less than 50 per cent of the original polyurethane. Now volatile gases are produced in small quantities but high boiling phosphorus compounds and short chain polyurea both generated in the "polymer" begin to volatilise out of the hot zone. At these temperatures, radicals may exist[83] and certainly some volatile material is likely to be the product of radical reactions[92].

Although the material continues to lose weight until 500° a stable residue which contains new bonds is forming before then. In contrast to charring in air, only small amounts of the phosphorus originally present in the polyurethane has been retained in the residue. It appears in the form of condensed phenylphosphonates and other cross-linked species.

Conclusions

Five conclusions about the thermal degradation of Polyurethane I have been drawn from the results of the studies described.

(A) Much of the thermal degradation reported in this chapter is highly characteristic of urethane polymers.

That is conventional mechanisms of initial degradation and many common secondary reactions occur in all samples of Polyurethane I when heated.

(B) The presence of copolymerised phosphorus modifies significantly the nature of thermal degradation of Polyurethane $I_{(0)}$. Every thermal

technique recorded the profound effect of phosphorus on the stability of polyurethane to heat.

(C) Phosphorus, acting in the form of an acid, facilitates urethane breakdown although it may not promote equally the three mechanisms of primary decomposition: (i), (ii) and (iii) (this chapter, page 135).

(D) Large quantities of carbon dioxide and pyrrolidines (from secondary amines) evolved by polyurethane with high phosphorus content suggest a shift in emphasis from mechanism (i) for $P.U.1_{(0)}$ to mechanisms (ii) and (iii).

(E) A mechanism which accounts for the features of thermal degradation studied in this chapter is summarised by Figure 6.XVIII.

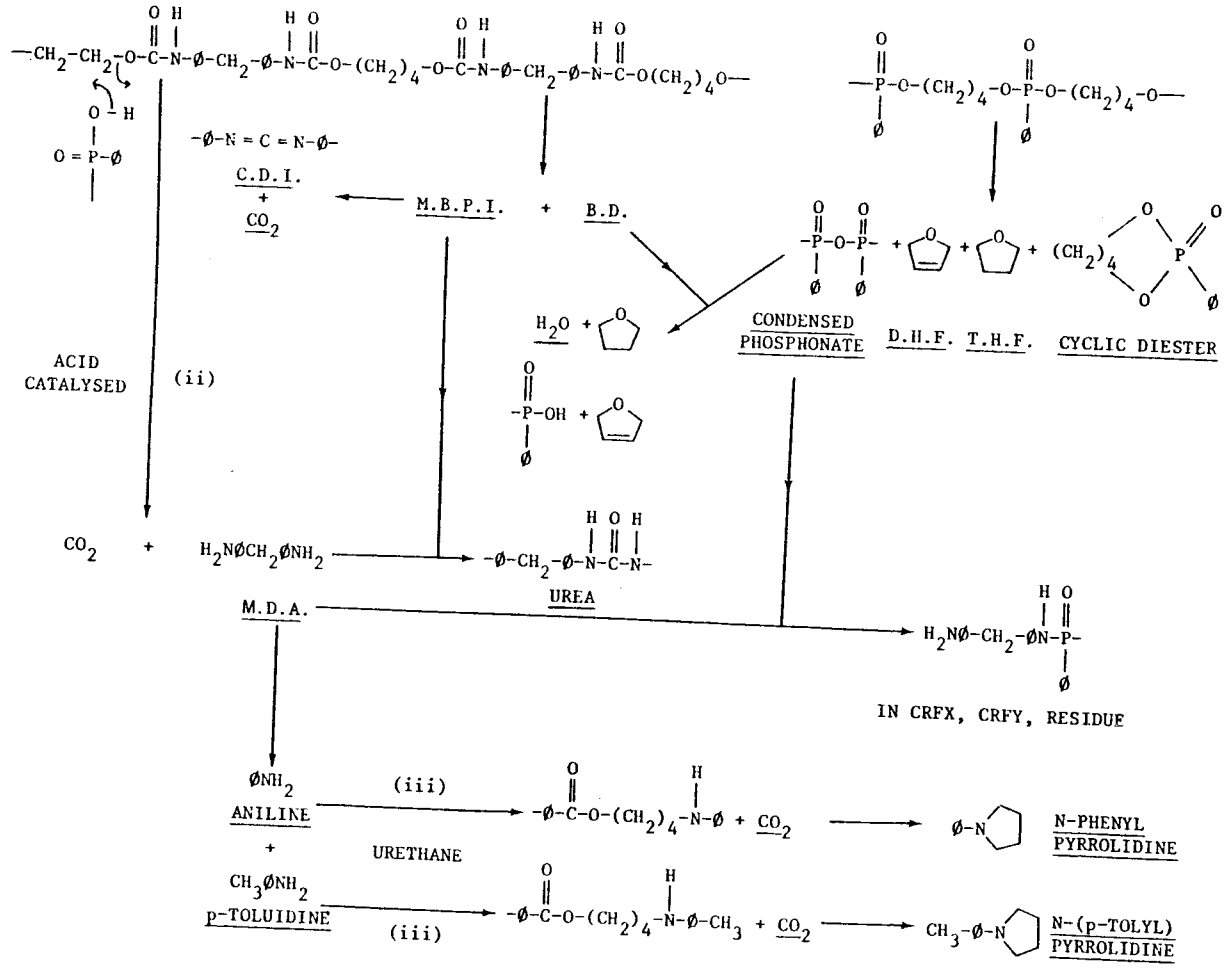


Figure 6.XVIII: Proposed Mechanism of Thermal Degradation of Polyurethane I

Ø represents the phenyl, ⬡, or phenylene, –⬡–, group

CHAPTER 7

THERMAL DEGRADATION OF POLYURETHANES 2, 3 AND 4

7.1 INTRODUCTION

Each polyurethane studied in this chapter represents a small structural modification to the phosphorus polyester segment of Polyurethane 1 (see Chapter 4). Although the polymers have not been studied as extensively as Polyurethane 1, gross differences in the properties of thermal degradation from those discussed in Chapter 6 can still be attributed to the modification in polymer structure. Two specific ideas governed the nature of the modifications made:

Polyurethane 2 was prepared to study the influence of phosphorus in a higher oxidation state on the thermal degradation of polyurethane. If phosphorus indeed acts as an acid to modify the path of thermal degradation of a polymer then copolymerised esters of phosphoric acid (a trifunctional acid) may be more effective agents than those esters of phosphonic acid (a difunctional acid).

Chapter 1 explained the significance of flammable volatile products of degradation to the burning cycle of polymers (page 6). With this in mind and knowing that unlike Polyurethane $1_{(0)}$ from M.B.P.I. and B.D. the polyurethane from M.B.P.I. and diethyleneglycol evolves negligible amounts of condensables during T.V.A.[94], it was decided to synthesise Polyurethanes 3 and 4 using polyphosphonates from P.P.D. and diethyleneglycol or triethyleneglycol.

Polyurethanes 2, 3 and 4 are treated in separate sections in this chapter.

7.2 THERMAL DEGRADATION OF POLYURETHANE FROM POLY[BUTYLENE PHENYL-PHOSPHATE], POLYURETHANE 2 (43)

T.G.A.

Figures 7.I and 7.II show that under a nitrogen atmosphere and vacuum with the usual rate of heating Polyurethane 2 loses weight in two distinct stages.

Under nitrogen, P.U.2 starts to lose weight around 240°. During the first stage of the process the rate of loss of weight reaches a maximum at 300° while the maximum rate in the second stage occurs at 355°. After 450° no further change occurs and a residue remains amounting to 20% of the original weight of polymer.

Although heating a sample under vacuum produces a T.G. curve of similar profile, initial loss of weight is observed at a lower temperature than before, namely at 210°. Again rate of loss of weight from the sample is a maximum at two temperatures, 300 and 333°. However the most significant difference between results of thermogravimetric analysis is the residue. Under vacuum a residue of only 4% of the weight of the original sample remains at 550°.

D.S.C.

Differential Scanning Calorimetry indicated that P.U.2 absorbs heat at several temperatures during thermal degradation. The D.S.C. trace of Polyurethane 2 in Figure 7.III shows an endotherm at 216°. That this represents the melting temperature of the polymer is implied by its full retention of weight and the absence of volatile products of degradation. In general the trace is complicated however at 270° where a distinct exothermic spike interrupts momentarily the endothermic processes of degradation. These endothermic reactions, recorded as a sample is heated, are complete by 450° which coincides with the final stages of weight loss under nitrogen.

T.V.A.

The T.V.A. trace in Figure 7.IV shows that evolution of volatile products of degradation from Polyurethane 2 begins around 230° reaching a maximum rate at 300°. After this the rate falls sharply until 360° when no further material volatile at room temperature is generated.

Noticeable separations between the 0, -45 and -75° traces appear during the early stages of degradation as a result of the quantity of aniline, water and D.H.F. produced. As expected carbon dioxide and

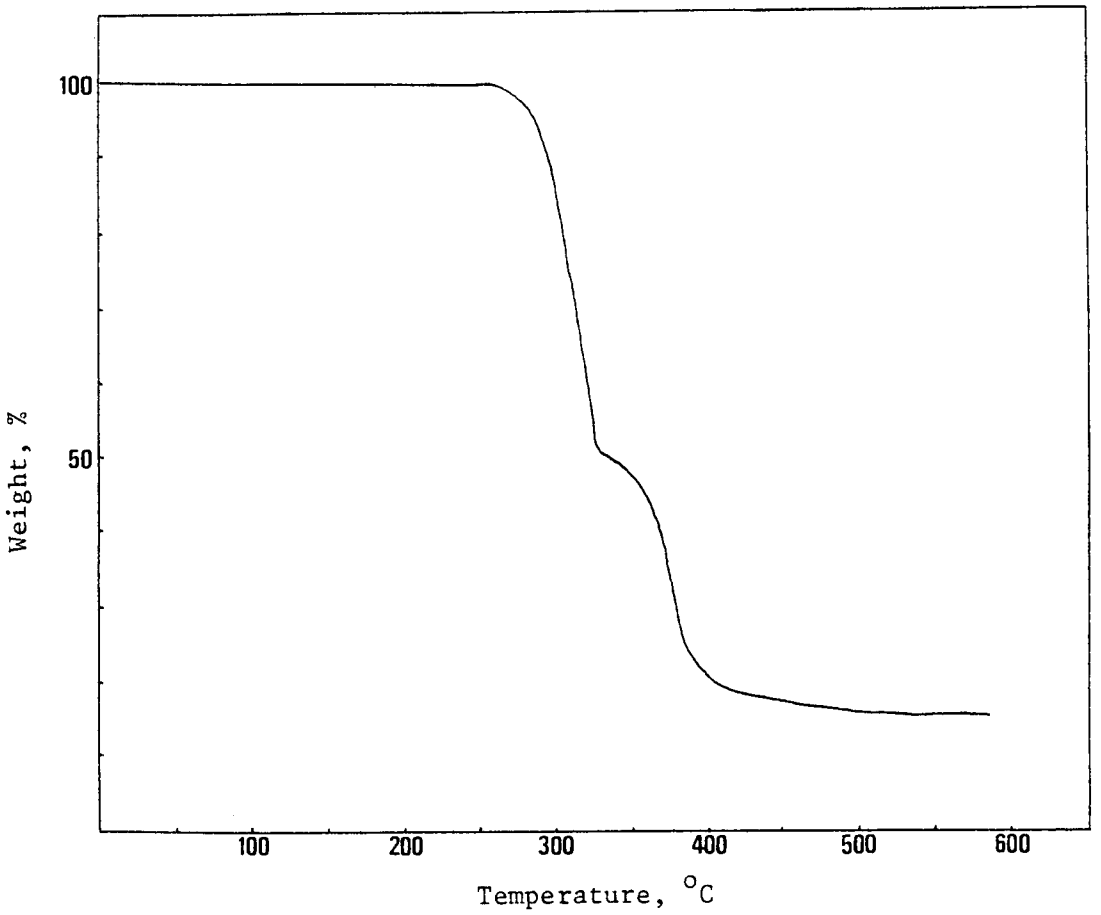


Figure 7.I: T.G. Curve of Polyurethane $2_{(44)}$ under Nitrogen

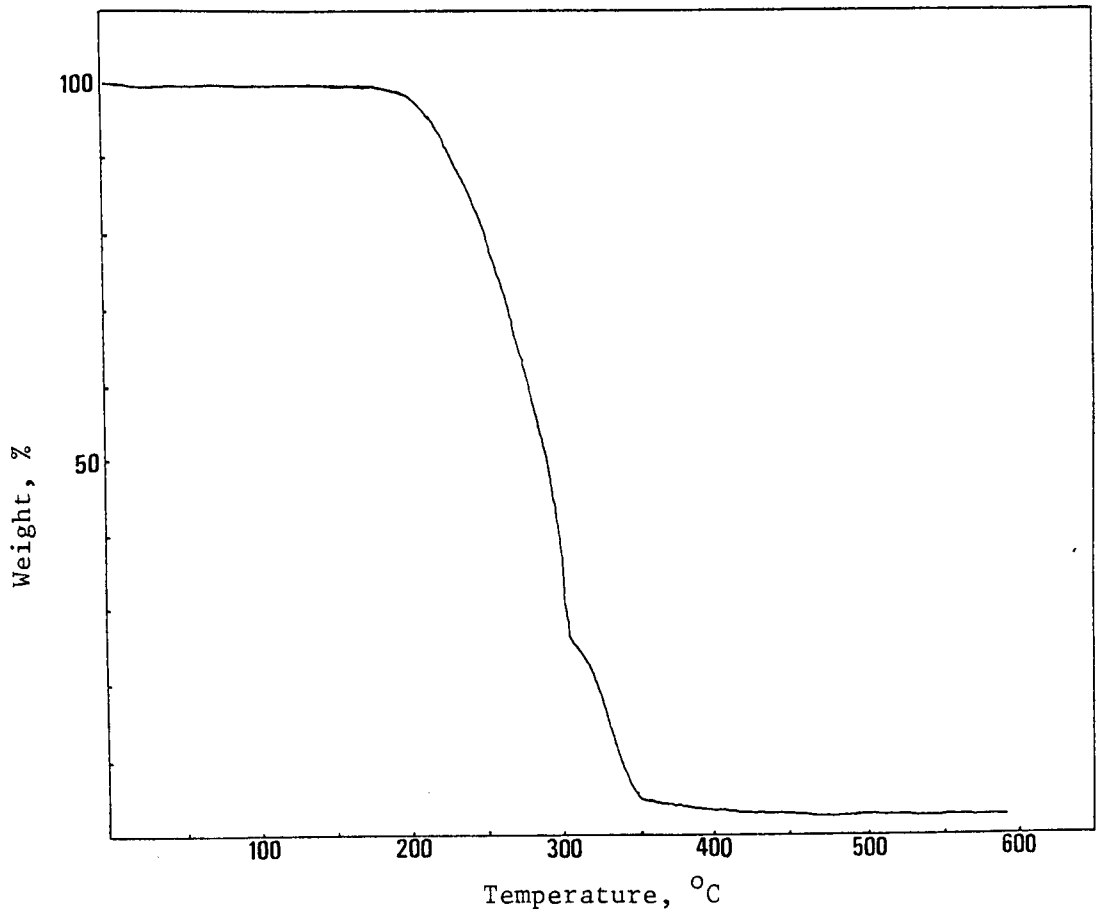


Figure 7.II: T.G. Curve of Polyurethane $2_{(44)}$ under Vacuum

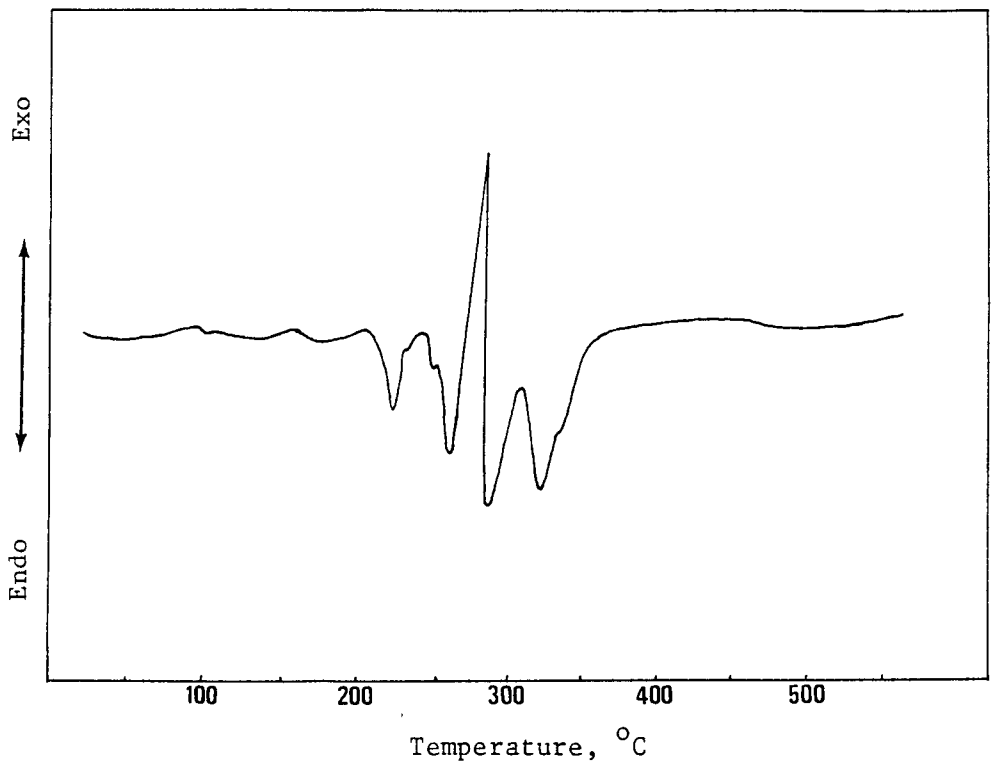
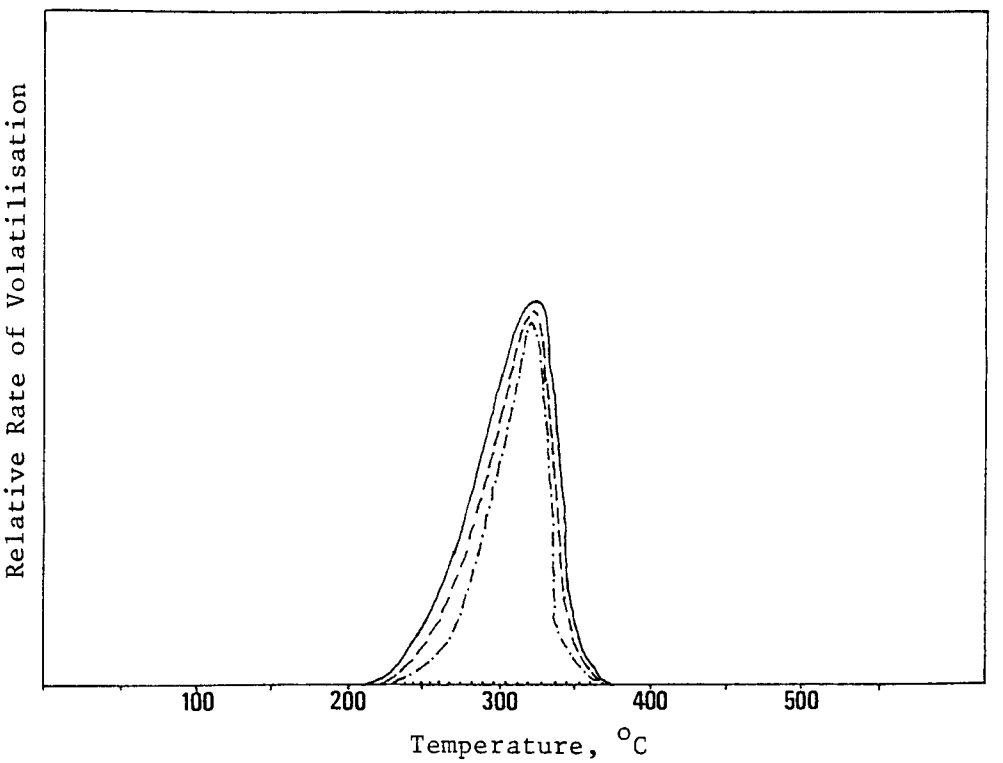


Figure 7.III: D.S.C. Trace of Polyurethane 2(44)



Trap Temperatures: —— = 0°, ---- = -45°, -·-·-·- = -75° and -100°, ····· = -196°

Figure 7.IV: T.V.A. Trace of Polyurethane 2(44)

tetrahydrofuran are also produced but the magnitude of response by the -100^{o} trace and the absence of a L.R.E. suggest that the quantity of T.H.F., although significant, is not sufficient to dominate the T.V.A. curve (see Chapter 6, Figure 6.IV).

Analysis of Products

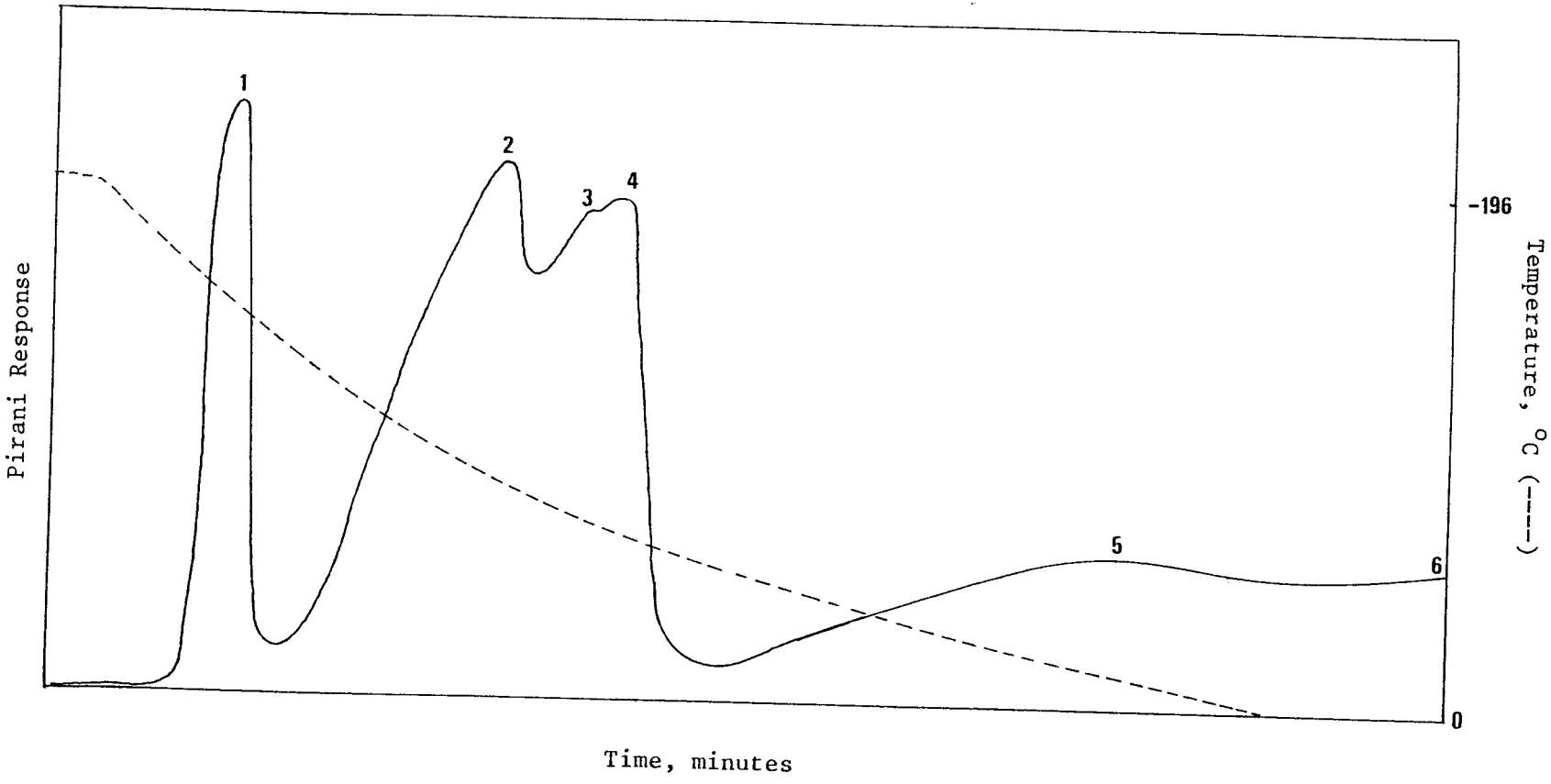
Subambient Thermal Volatilisation Analysis: Figure 7.V shows that subambient separation of the volatile products after thermal degradation of 60 milligrams of Polyurethane 2 indicates that at least six compounds are present. Infrared analysis only was performed to identify the fractions which included CO_2, T.H.F., D.H.F. and water. Two high boiling fractions (5 and 6) contained aniline and N-phenylpyrrolidine respectively although other minor products were present.

Cold Ring Fraction: All high boiling products of thermal degradation which condensed at the cooler walls of the thermal volatilisation tube were solids and could be removed easily for analysis. Since individual cold ring fractions did not separate in the T.V. tube as before (Chapter 6, page 113) samples were taken from different areas of the cold ring deposit and analysed by I.R. M.B.P.I., polyurea and carbodiimide were identified. The deep red colouring throughout most of the cold ring and infrared absorptions by some samples ($3300cm^{-1}$ and $1500-1560cm^{-1}$) suggested from experience that amine functions were present.

Residue: Microanalysis was performed on residues collected after thermal volatilisation of Polyurethane 2 and chars produced by heating isothermally samples in air at 300^{o} for 45 minutes. The average phosphorus contents of residues and chars are recorded in Table 7.i. The amount of phosphorus recovered is also expressed as a fraction of that present in the original polymer.

Partial Thermal Degradation

For an indication of which structures in Polyurethane 2 are most sensitive to heat, a thin film of polymer was prepared and heated in the T.V. apparatus. Degradation was interrupted shortly after the film began to release volatile products. Infrared analysis showed negligible loss of urethane absorption by the film but total loss of phenoxyphosphorus (⟨O⟩—O-P-) absorption (see Chapter 4, Table 4. iv). While no evidence of chain scission in the polyester region was found it is clear that the regions of polymer with high phosphorus concentrations provide the sites of initial thermal degradation.



Key to Products: 1 = Carbon dioxide, 2 = T.H.F., 3 = D.H.F., 4 = Water, 5 includes aniline, 6 includes N-phenylpyrrolidine

Figure 7.V: Subambient Trace of Polyurethane 2(44)

Table 7.i: Phosphorus Contents of Residue and Char from Polyurethane 2(44)

	Weight as a percentage of P.U.2	Phosphorus Content by weight (%)	Content expressed as a percentage of Phosphorus present in P.U.2
Residue	4.0	2.41	4.08
Char	39.2	1.73	28.73

7.3 THERMAL DEGRADATION OF POLYURETHANE FROM POLY[OXYDIETHYLENE PHENYLPHOSPHONATE], POLYURETHANE 3

T.G.A.

Under vacuum or nitrogen, Polyurethane 3 loses most of its weight over a small temperature range. Figure 7.VI indicates the common situation where loss of weight from polymer is consistently greater under vacuum than nitrogen.

When heated under dry dynamic nitrogen, P.U.3 starts to lose weight near 250°, the rate of loss reaching a maximum at 308°. Although not obvious from the thermogram, the first derivative of the T.G. curve indicates rate of loss of weight achieves a second maximum around 450°. After 550° no further change in weight occurs and a residue, 24% of the original mass of polymer, is left.

The thermogravimetric curve from a sample in vacuum is more dramatic. Decrease in weight of polyurethane starts around 210° with loss of weight accelerating to a maximum rate on two occasions at 310° and 460°. By 550° a residue, 7% of weight of the starting material, remains.

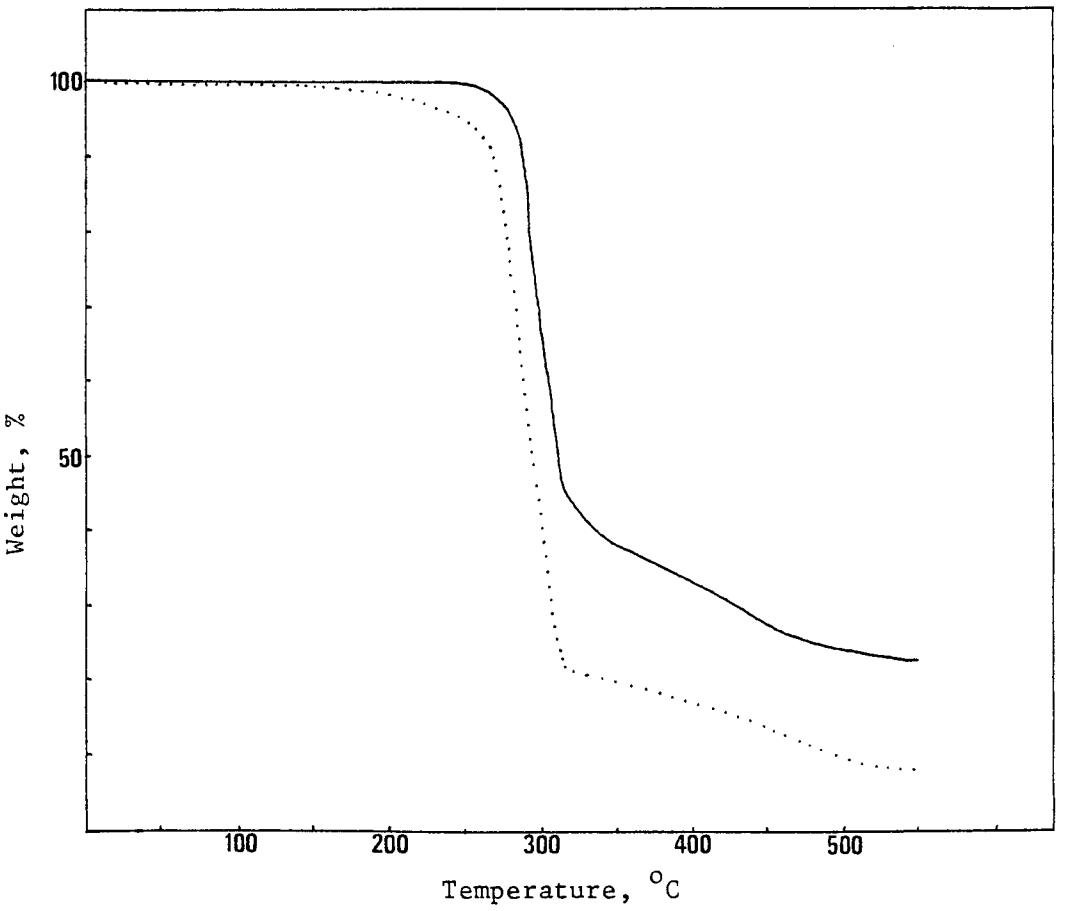
D.S.C.

Reactions which occur during thermal degradation of P.U.3 produce the net endothermic decomposition shown in Figure 7.VII. From 275° the polymer absorbs large amounts of heat and experiences a simultaneous sharp loss of weight. Near 295° the endotherm is interrupted as a short-lived exothermic reaction returns the system momentarily to thermal equilibrium with its environment, however endothermic processes immediately predominate and heat continues to flow into P.U.3 up to a temperature of 325°. Thereafter only minor differences in temperature between polymer and its surroundings occur.

T.V.A.

According to Figure 7.VIII, as a temperature of 215° is approached, volatile products from degradation of Polyurethane 3 appear. The rate of evolution of the volatile materials reaches a maximum near 285° but degradation of the sample beyond 305° produces condensables in only small amounts.

The pirani response between 110 and 215° indicates the presence of volatile material released by P.U.3 below degradation temperatures. The material, identified as dimethylacetamide, was solvent occluded in



T.G. Curves: ——— = under nitrogen

····· = under vacuum (continuous pumping)

Figure 7.VI: T.G. Curve of Polyurethane 3(34)

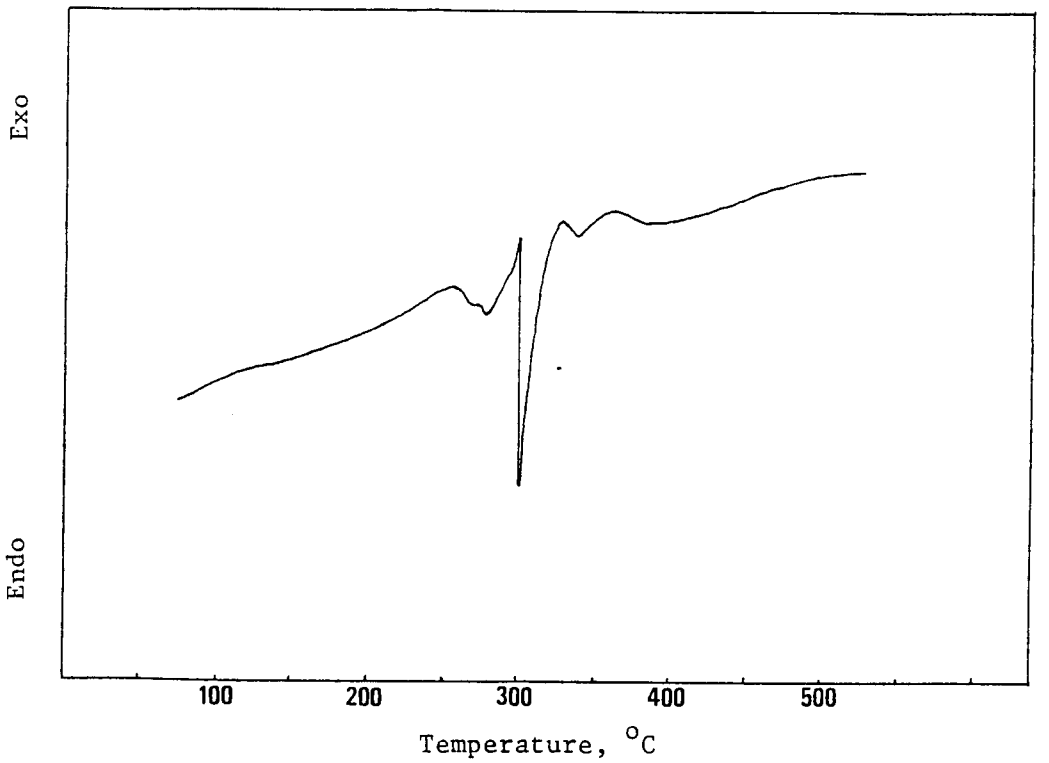
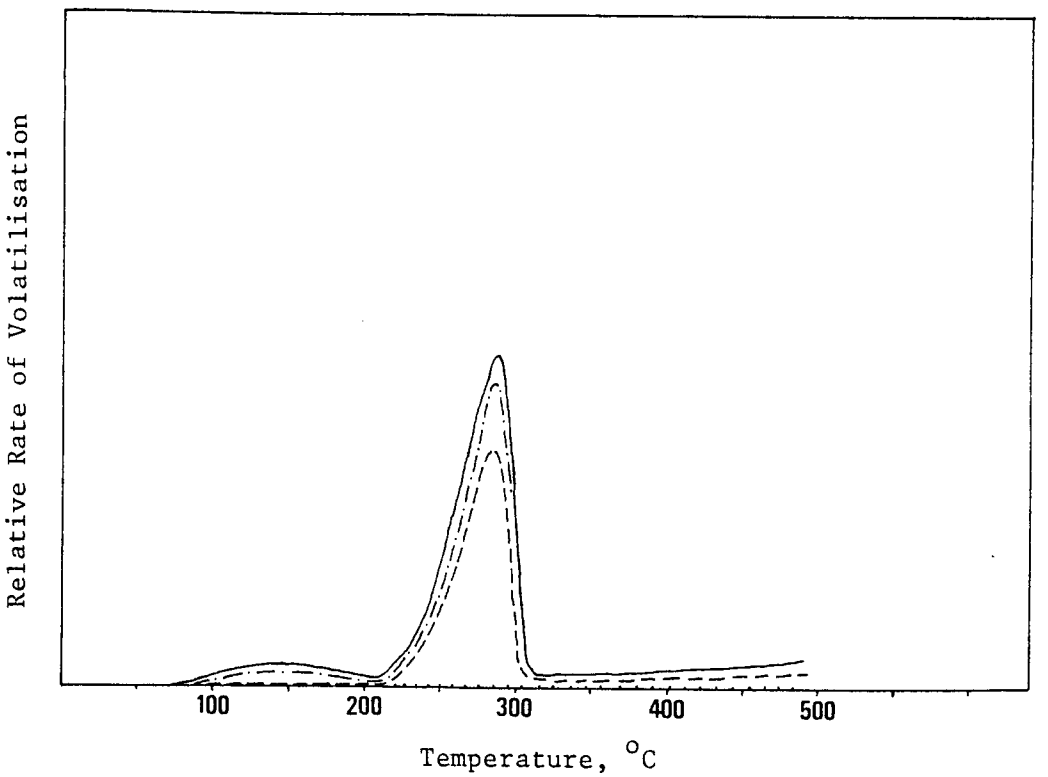


Figure 7.VII: D.S.C. Trace of Polyurethane 3(34)



Trap Temperatures: —— = 0° and -45°, -·-·- = -75°,
---- = -100°, ····· = -196°

Figure 7.VIII: T.V.A. Trace of Polyurethane 3(34)

the polyurethane during polymerisation, its removal by reprecipitation methods being prevented by poor solubility of the polymer in organic solvents (Chapter 3, page 47).

Analysis of Products

Subambient Thermal Volatilisation Analysis: The subambient trace of volatile products from the thermal volatilisation of Polyurethane 3 indicates that at least six compounds are present. Fractions 1 to 5 in Figure 7.IX were shown by a combination of mass spectrometry and I.R. analysis to contain carbondioxide, T.H.F., D.H.F., water and D.M.A. respectively. Fraction 6 was not identified successfully.

Quantitative Analysis of CO_2 and T.H.F.: Since the object of the synthesis of P.U.3 and P.U.4 was to prepare polyurethane which contained phosphorus yet evolved small quantities of volatile, flammable material during decomposition, the quantitative measurement of T.H.F. after thermal degradation was particularly relevant. Investigations showed when Polyurethane 3 is heated the amounts of T.H.F. and carbon dioxide formed are significantly smaller than from Polyurethane 1 containing equivalent amounts of phosphorus. The results are summarised in Table 7.ii.

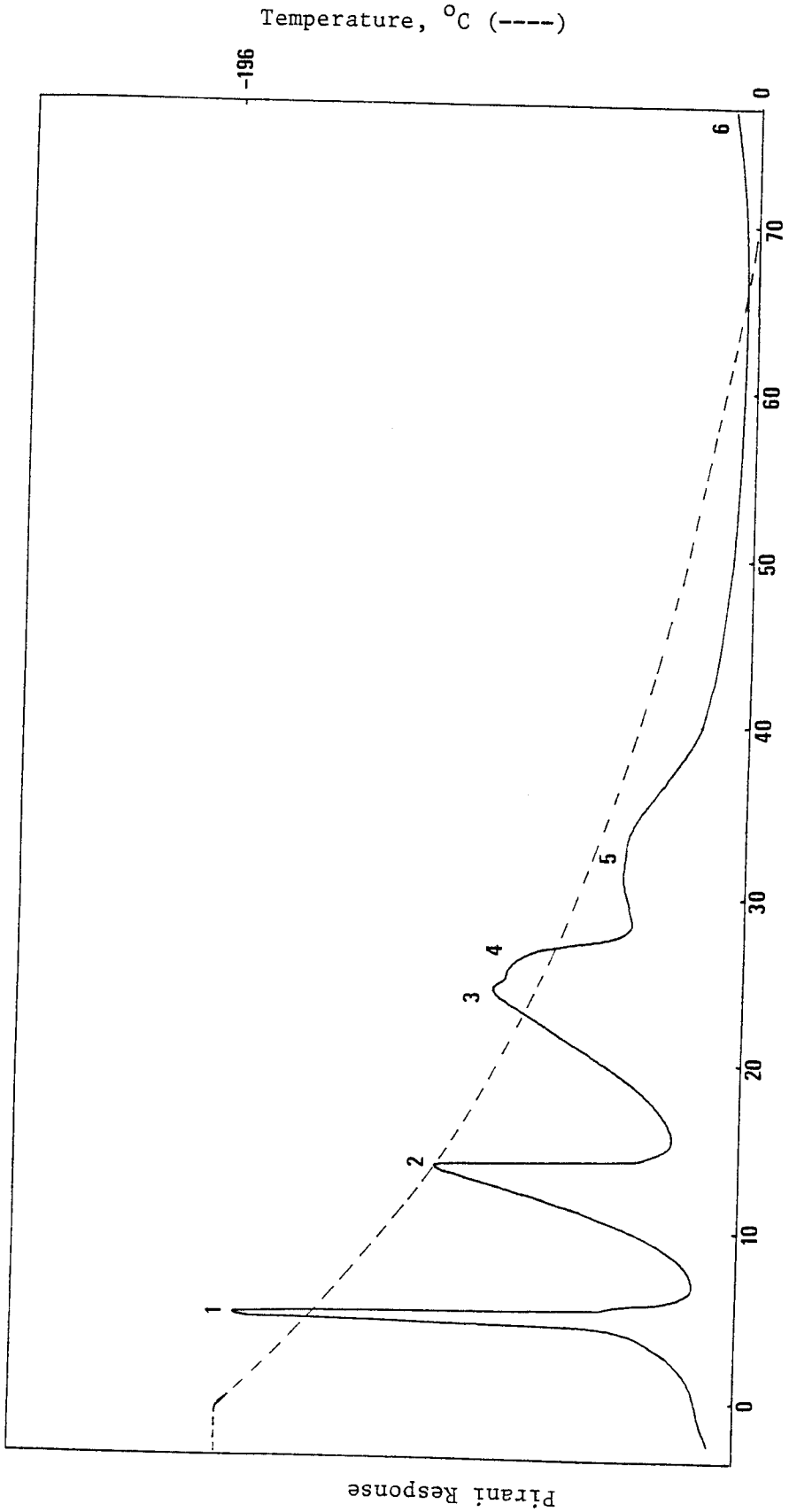
Residue: Residues from samples after thermal volatilisation analysis and chars of the polyurethane were analysed for phosphorus. Results in Table 7.iii indicate the amount of phosphorus found in material remaining after degradation or charring does not account fully for the amounts known to be present initially in Polyurethane 3.

7.4 THERMAL DEGRADATION OF POLYURETHANE FROM POLY[(ETHYLENE BIS(OXY))-DIETHYLENE PHENYLPHOSPHONATE], POLYURETHANE 4

T.G.A.

T.G. curves of Polyurethane 4 studied under dynamic nitrogen atmosphere and vacuum are presented in Figure 7.X. The polymer is stable under nitrogen to ~250°. However as the temperatures increase the polyurethane loses weight rapidly until 310° when material amounting to 50% of original weight of sample has escaped. This temperature corresponds closely to maximum rate of loss of weight but shortly after, around 400°, only minor weight changes still occur until finally a residue 19% of the original mass is left.

The polyurethane begins to lose weight under vacuum at temperatures lower than those required for degradation in a nitrogen atmosphere.



Key to Products: 1 = Carbon dioxide, 2 = T.H.F., 3 = D.H.F., 4 = Water, 5 = D.M.A., 6 = Unidentified

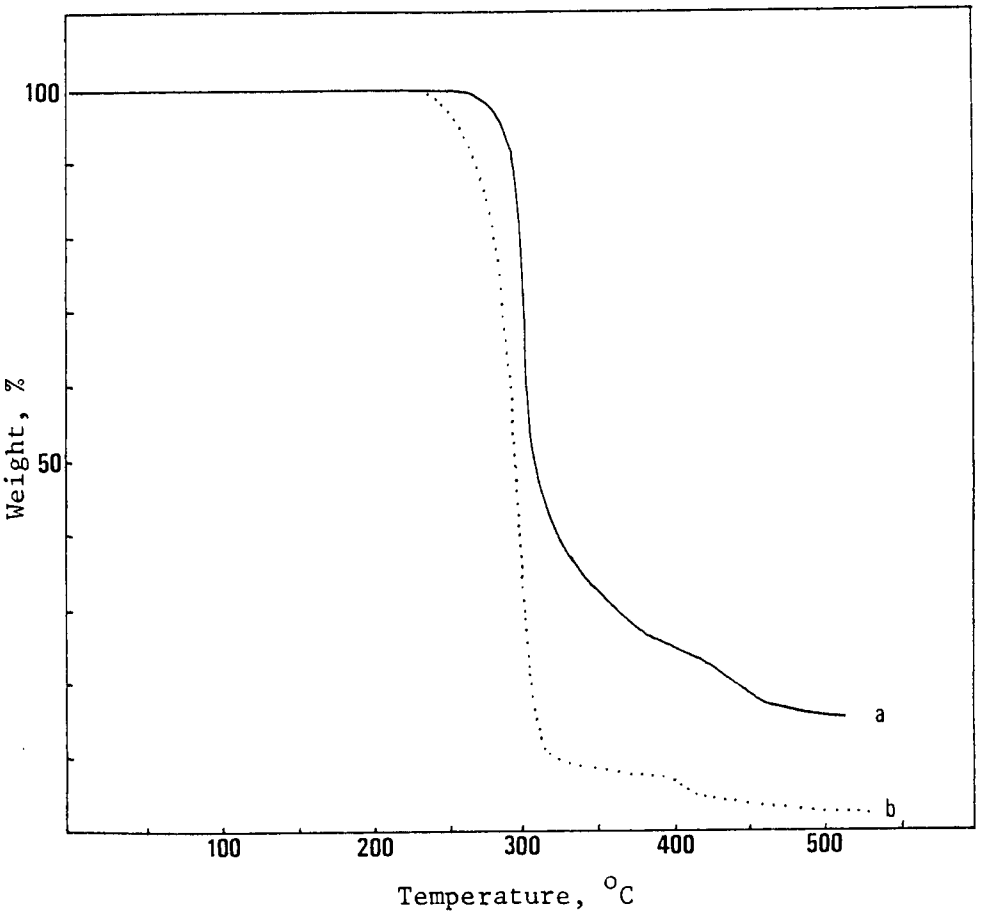
Figure 7.IX: Subambient Trace of Polyurethane 3(34)

Table 7.ii: Quantities of Carbon dioxide and T.H.F. from Polyurethanes $3_{(34)}$ and $4_{(31)}$

	Moles Carbon dioxide/g Polyurethane			Moles T.H.F./g Polyurethane		
	Observed	Calculated	% Yield	Observed	Calculated	% Yield
P.U.$3_{(34)}$	.000975	.00403	24.2	.000529	.00193	27.4
P.U.$4_{(31)}$	.000847	.00670	12.6	.000615	.00303	20.3

Table 7.iii: Phosphorus Contents of Residues and Chars from Polyurethanes 3(34) and 4(31)

		Weight as a Percentage of Polyurethane	Phosphorus Content by Weight (%)	Content expressed as a Percentage of Phosphorus present in Polyurethane
Polyurethane 3(34)	Residue	7	8.23	15.5
	Char	52.2	4.80	67.4
Polyurethane 4(31)	Residue	3	7.85	7.7
	Char	41.7	4.71	64.2



T.G. Curves: ——— = under Nitrogen, a

····· = under Vacuum (continuous pumping), b

Figure 7.X: T.G. Curves of Polyurethane 4(31)

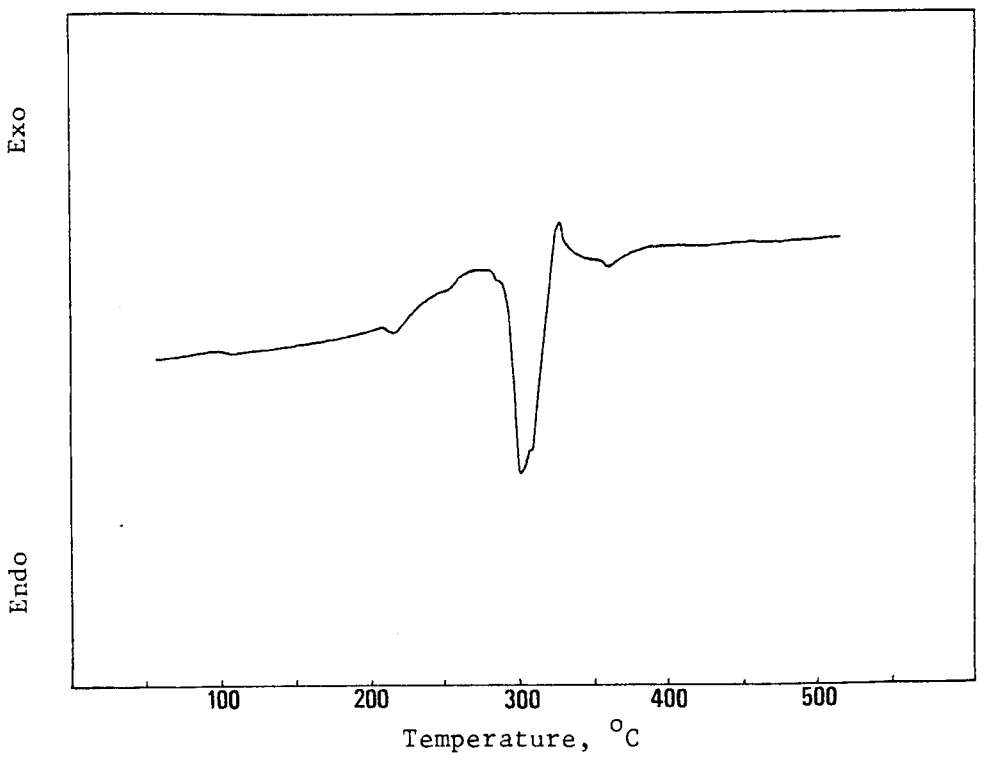


Figure 7.XI: D.S.C. Trace of Polyurethane 4(31)

88% of the sample is lost in a single stage which finishes around 350°. However a further small change is recorded before 500° at which temperature a residue 3% of original sample mass is left. Maximum rates of loss of weight during the two stages occur at 310 and 415°.

D.S.C.

Figure 7.XI shows that the D.S.C. trace of P.U.4 is relatively simple. When the polymer is heated to ~260° endothermic processes of degradation commence and continue to absorb heat until ~310°. Thereafter reactions of thermal degradation within the material produce no net endothermic or exothermic effect despite changes in weight known to occur.

T.V.A.

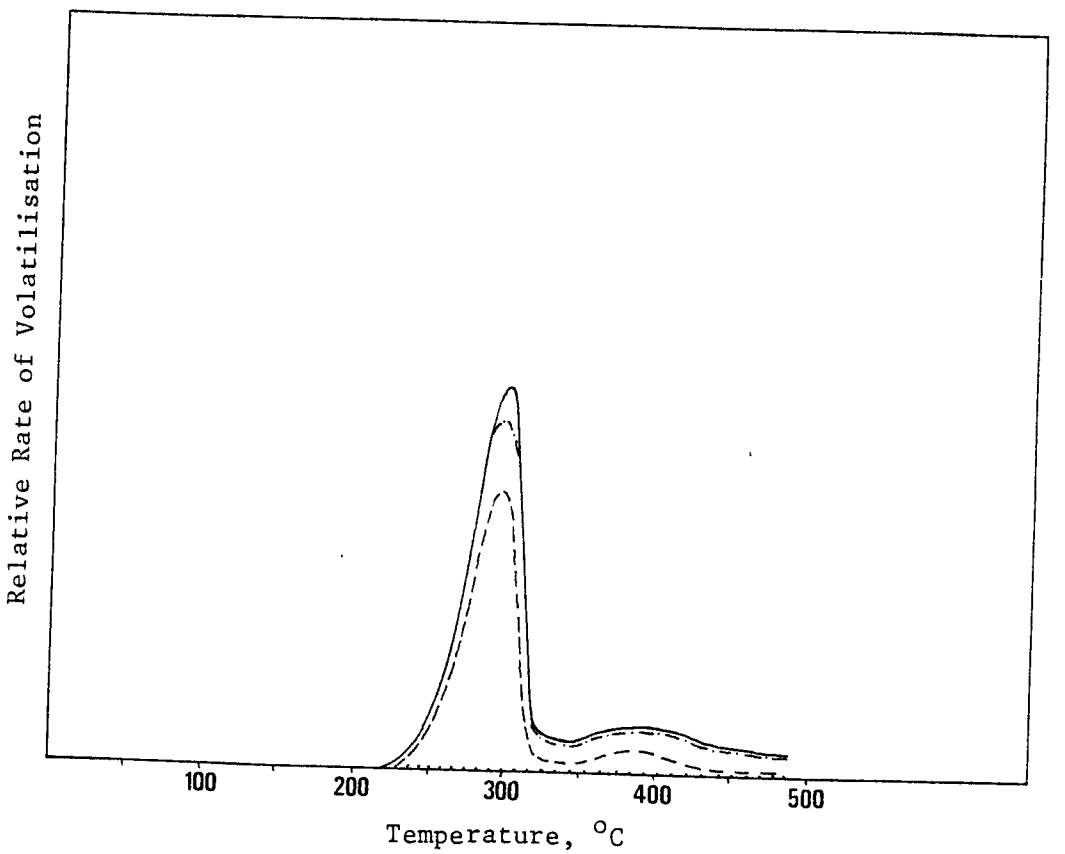
The T.V.A. trace of Polyurethane 4 in Figure 7.XII shows volatile products of degradation are detected after 230°. The trace, similar to that of P.U.3, illustrates that the rate of evolution of volatile material drops sharply after reaching a maximum around 290° but increases slowly again to 390°. These two periods of evolution of volatile products centred around the temperatures mentioned correspond to the start of major losses of weight from the polymer (see Figure 7.X(b)).

Analysis of Volatile Products

Subambient Thermal Volatilisation Analysis: Subambient separation of volatile products of degradation from the polyurethane produced five fractions as illustrated in Figure 7.XIII. The first four fractions to distil were identified by their infrared spectra as carbon dioxide, T.H.F., D.H.F. and water. The identity of the final fraction, 5, was not determined.

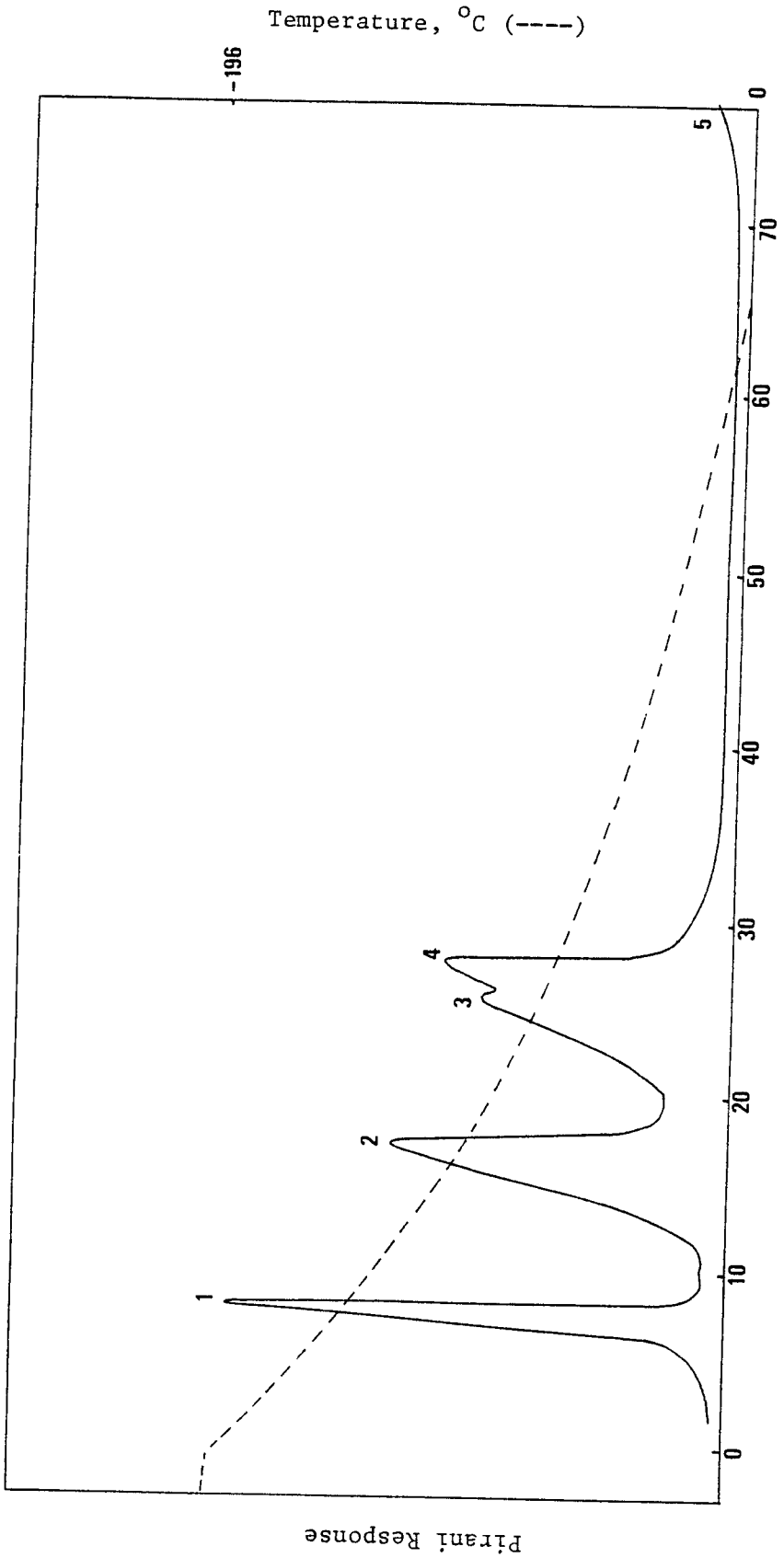
Quantitative Analysis of CO_2 and T.H.F.: A reduction in the amount of gases evolved by Polyurethane 4 compared with the corresponding member of the Polyurethane 1 series was again apparent. Values given in Table 7.ii are moles of carbondioxide and tetrahydrofuran recovered from 1 gram of P.U.4 and are also expressed as percentages of theoretical amounts based on polymer composition described in Chapter 4.

Residue: Analysis of residue and char from the polyurethane was confined to measurement of sample weight and phosphorus content. Results are given in Table 7.iii.



Trap Temperatures: —— = 0° and -45°, -·-·- = -75°,
---- = -100°, ····· = -196°

Figure 7.XII: T.V.A. Trace of Polyurethane 4 (31)



Key to Products: 1 = Carbon dioxide, 2 = T.H.F., 3 = D.H.F., 4 = Water, 5 = Unidentified

Figure 7.XIII: Subambient Trace of Polyurethane 4 (31)

7.5 DISCUSSION

A discussion of thermal degradation of Polyurethanes 2, 3 and 4 may be most meaningful if compared with that of Polyurethane 1, where the mechanisms involved have been identified to a large extent, in the hope of relating some differences to more fundamental origins. Before this, however, comparison of P.U.2, 3 or 4 with one specific member of Polyurethane 1 series must be justified.

Simply from phosphorus content it appears:

1. the prepolymers containing phosphorus may not copolymerise as efficiently as M.B.P.I.;
2. the relative reactivities of the prepolymers used during synthesis of Polyurethanes 1-4 may be different.

Thus it may be unfair to appraise Polyurethane $2_{(43)}$ by comparison with Polyurethane $1_{(44)}$ but more realistic to compare Polyurethanes 2, 3 and 4 with Polyurethane 1 which has similar content of phosphorus. Thus P.U.$2_{(43)}$ should be compared with P.U.$1_{(11)}$ and in fact the two polymers show many similarities during thermal degradation.

Polyurethane 2: Although it could be argued that the number of differences in thermal properties between P.U.$1_{(11)}$ and P.U.2 are equal to the number of similarities the latter are represented by the more outstanding features of thermal degradation. For example the sharp exothermic spike recorded by D.S.C. shortly after degradation of P.U.2 commences is observed at similar temperatures when P.U.$1_{(11)}$ is studied. T.G. shows appreciable loss of weight from both P.U.$1_{(11)}$ and P.U.2 begins near 240°, profiles of the subsequent T.G. curves being very similar (Chapter 6, page 97, and this chapter, page 147). Residues are of similar order ~20% and much of weight loss is accounted for by volatile products of degradation, indicated qualitatively by pirani response during T.V.A. Separation and analysis of products from thermal degradation of Polyurethane 2 prove amounts of aniline and N-phenylpyrrolidine easily detected during subambient separation are produced while little if any p-toluidine and N-(p-tolyl)pyrrolidine is generated. This situation is reminiscent of Polyurethane 1 which contains small amounts of copolymerised phosphorus (Chapter 6, Table 6.iv).

The role played by phosphorus during and its distribution among final products after thermal degradation again compare between P.U.$1_{(11)}$ and P.U.2. Initial thermal degradation seems to be located in polyester regions of the polymers with phosphorus polyester and probably urethane segments undergoing acid catalysed degradation. After decomposition of

both polyurethanes products which contain phosphorus are restricted to cold ring regions and residue, the latter accounting for a small fraction of the known total amount of phosphorus.

To summarise, the similarity of evidence from studies of thermal degradation of Polyurethane 2 to that of Polyurethane $1_{(11)}$ infers that a mechanism of degradation resembling that proposed in Chapter 6, Figure 6.XVIII, may operate. However in complete contrast to the stability of the phosphorus-phenyl bond in P.U.1, phosphorus atoms apparently lose phenoxy groups early during thermal degradation of P.U.2 and any mechanism proposed to account for decomposition of this polymer must include this feature.

Polyurethanes 3 and 4: Results from investigation of Polyurethanes 3 and 4 show noticeable deviations from properties of degradation of Polyurethane $1_{(44)}$ which contains similar amounts of phosphorus. Not only is the number of volatile products from degradation of P.U.3 and P.U.4 less than that from P.U.1 but as anticipated the quantities of condensables released are far smaller in the two former cases. The two polyurethanes lose little stability to heat for the concentration of phosphorus which is copolymerised and produce sizeable chars containing phosphorus which accounts for over 60% of the amount known to be present initially in the polymers.

One small piece of information concerning Polyurethane 1 was extracted from results of analysis of subambient fractions from P.U.3 and P.U.4. Clearly the only source of D.H.F. and T.H.F. in these polymers was butylene links present in the urethane segment thus identification of both compounds among the subambient fractions demonstrated when butylene links were present in urethane and polyester segments (Chapter 5, page 83) both cyclic ethers would be generated. That is Polyurethane 1 with or without copolymerised phosphorus will generate both condensables from appropriate sites in its polyester and urethane regions.

With the information available, sufficient to highlight distinctions from thermal degradation of P.U.1 and P.U.2 but insufficient in detail it would be difficult to suggest a mechanism to account for thermal degradation of P.U.3 and P.U.4; however this work and literature[10,82,88] relate a sameness in the way in which phosphorus modifies thermal degradation of urethanes. It is likely therefore that, under the influence of copolymerised phosphorus, urethane segments in the two polymers degrade in the manner described in Chapter 6, Figure 6.XVIII.

However detailed analysis of cold ring fractions together with isothermal degradation studies would be required to indicate mechanisms leading to products from the polyester segments.

So in conclusion although incorporation of phosphorus into the backbone of polyurethane causes dramatic changes to the mechanism of degradation Chapter 7 has shown that factors other than the concentration of copolymerised phosphorus can modify significantly the features of degradation some perhaps having consequences on the final flammability of the material.

CHAPTER 8

DISCUSSION AND CONCLUSIONS

The Flammability of Plastics

Some aspets of the mechanism of thermal degradation of polyurethanes containing copolymerised phosphorus have been both revealed and confirmed by this work. However any assessment of the performance of these materials during a real fire situation, using the information acquired, would at best be qualitative.

In an attempt to establish laboratory scale tests which indicate the flammability of plastics, the American Society for Testing and Materials (A.S.T.M.) has designed various methods which measure characteristics of a burning polymer. These tests which classify materials in terms of smoke density from burning (A.S.T.M. D2843-70), critical oxygen index (A.S.T.M. D2863-70), flame spread (A.S.T.M. 1692-67) and so on do provide an accurate picture of the flammability of polymer samples studied in a laboratory. Manufacturers of laboratory instruments now market several designs notably the high temperature oxygen index module which conform to A.S.T.M. specifications and it is claimed that a combination of these techniques will afford polymer flammability data[95].

Unfortunately the flammability properties of a polymer under laboratory scrutiny may not reflect those of the same polymer under operating conditions which may be different again from its fine performance. To this effect the Annual Handbook of A.S.T.M. Standards includes clauses such as "Correlation with flammability under actual use conditions is not necessarily implied"[96] and in some instances the order of flammability as defined by standard tests for a series of plastics appears to be reversed in real fire situations[9].

It is the case then that prediction of the fire hazard presented

by polymers in their everyday use from data gathered in the laboratory is difficult and sometimes unreliable. Although this shortcoming implies that only trial and error methods can guarantee to improve flame resistance of polymers, knowledge of the influence of flame retardant additives or reactives on the mechanism of thermal degradation of polymers can help significantly to improve this situation.

Comparison of the mechanism of thermal degradation of a polymer with its performance in burning situations will begin to reveal features which are important to flame resistance. (Typically these features are amount of char, quantity of retardant retained in the char, synergism, the quantity of volatile products, flammable and toxic, the nature of the retardant whether additive or reactive.) Modifications in the molecular scale aimed at improving these properties can be judged when the mechanism of thermal degradation is known in detail and therefore more effective steps can be taken which are likely to improve fire resistance on the macroscopic scale.

So the elucidation of the mechanism of thermal degradation of polymers is important in the field of flame resistant polymers. It will play a role in the improvement and development of such materials and with a little experience offer an equal or better method of assessing flame resistance than many standard tests.

Mechanism of Thermal Degradation of Polyurethanes containing Phosphorus

Details of the mechanism of thermal degradation of Polyurethanes 1, 2, 3 and 4 have been discussed in Chapters 6 and 7 and it is clear that phosphorus affects the mechanism of degradation of polyurethanes. There is little doubt that the element acts in the form of an acid[12,13,91] and in fact the blend of Polyurethane $1_{(0)}$ with phenylphosphonic acid degrades thermally to give products virtually identical to those described in Chapter 6.

Although investigation of several polyurethanes similar to P.U.2 containing a range of phosphorus : urethane ratios would have been more informative it appears that no advantage is gained through use of phosphorus with its highest oxidation number. Further, some studies of thermal degradation using static air atmospheres indicated that products of degradation are similar to those collected under vacuum. Thus the presence of acid in polyurethane appears to be the factor critical to the nature of its thermal degradation and by comparison other structural modifications produce modest effects.

Appraisal of Flame Resistance of Polyurethanes 1, 2, 3 and 4

As mentioned earlier in this chapter a detailed study of the mechanisms of thermal degradation of polyurethanes is important to the evaluation of their flammabilities. However it does not entirely solve the problem of relating properties measured in a laboratory to performance in a fire. Although this final step is empirical, a survey of the amount of char formed by each polyurethane, the levels of phosphorus after charring, the natures and quantities of volatile products from thermal degradation indicates the polymers likely to exhibit improved flame resistance. Polyurethane 1 with high concentrations of phosphorus, Polyurethane 3 and Polyurethane 4 show most promise and deserve further investigation. Since much of the thermal degradation of P.U.3 and P.U.4 resembles that of $P.U.1_{(44)}$ and $P.U.1_{(54)}$ despite the use of smaller amounts of phosphorus it appears a knowledge of the mechanism of thermal degradation of Polyurethane 1 has been used to make a successful modification to the polymer structure.

Suggestions for Future Work

It is the nature of scientific research that its results should suggest further avenues of investigation.

A natural development of this work would include analysis of products from degradation under nitrogen[80,88] and air, although this can present practical problems.

Although this research was confined to phosphorus flame retardants a combination of elements is often used in practice. This exploits the synergistic effect which some retardants exhibit and the mechanism of degradation of polyurethane containing such combinations would merit close attention.

This project has shown that polyurethanes lose some stability to heat when the inorganic phosphorus is incorporated in the polymer backbone. Similar investigations of corresponding N-substituted polyurethanes containing copolymerised phosphorus should indicate an improvement in thermal stability[81] and the role of the urethane hydrogen in the mechanism of degradation revealed more fully.

The nature of the phosphorus polyester segment can also be changed from polyphosphonate to polyphosphine or polyphosphine oxide with a view to increasing thermal stability[65]. This may be done with no loss of flame retardant efficiency from the phosphorus despite an oxidation state as low as -3[13].

To conclude it seems reasonable that a mixture of scientific research and trial and error will steadily improve the flammability properties of materials such as polyurethane. The common retardants used at present often produce detrimental changes in the physical properties of the polymers and compromises between performance and flame resistance have to be finely balanced. Any progress in imparting fire retardant properties to polymers must also be judged by effects on mechanical properties and such studies must be an integral part of any comprehensive study.

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